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Response of Portable VOC (Volatile Organic Compounds) Analyzers to Chemical Mixtures

Radian Corp.
Austin, TX

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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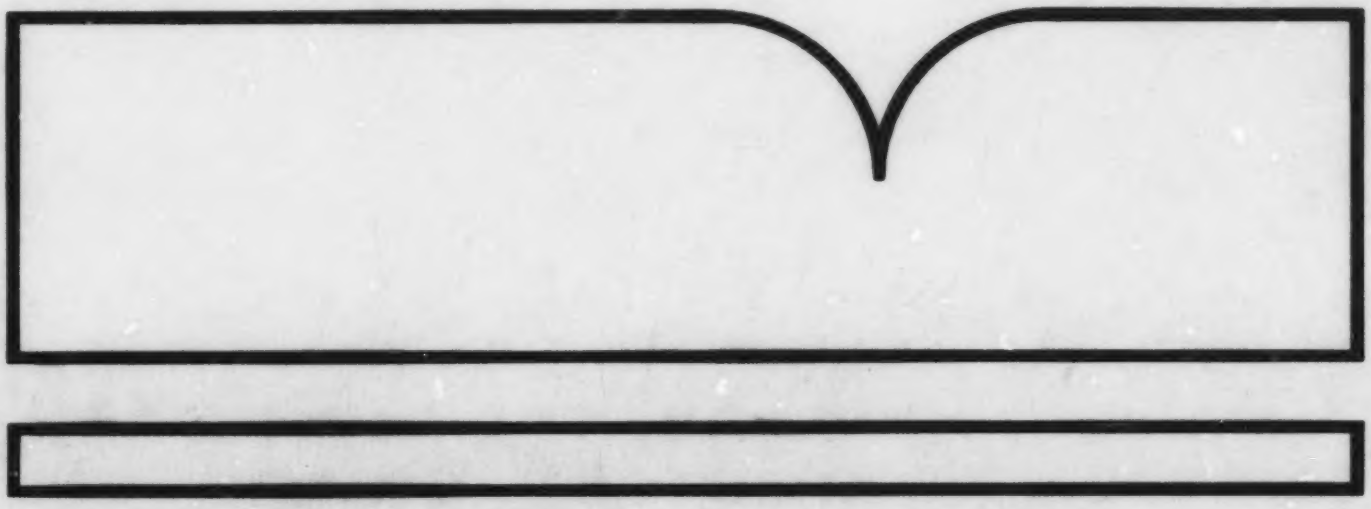

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RESPONSE OF PORTABLE VOC ANALYZERS TO CHEMICAL MIXTURES

Final Report

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SECTION 1

INTRODUCTION AND SUMMARY

Portable VOC (Volatile Organic Compounds) analyzers have been widely used in the identification of fugitive emission sources, a process commonly called "screening". Screening is important both in research to develop emission factors and in proposed regulatory monitoring of fugitive emissions. While these VOC analyzers will respond to most organic vapors, they respond with varying sensitivity to different chemical species.

Radian Corporation performed a laboratory evaluation of the response characteristics of two common VOC analyzers (the Century Systems OVA-108 and the J. W. Bacharach TLV Sniffer) to a large variety of individual organic compounds in air. The results of this EPA funded study are available from the National Technical Information Service as NTIS #PB81-136194.

This report presents the results of testing in the area of chemical mixtures. The total data base reported here includes response data on nine binary chemical combinations of acetic acid, acetone, chloroform, cyclohexane, benzene, methanol, and methyl ethyl ketone plus one ternary combination. This report presents only the response data and the results of fitting these data to various mathematical models. Details of the experimental methodology can be obtained from the above cited report on individual response factors.

The results of these analyses show that the response to a binary chemical mixture falls between the responses of the two individual chemicals at the total concentration of the mixture. This indicates that synergistic effects are weak and suggests that some form of interpolation or weighted average can be used to predict the response of the mixtures based on individual chemical response characteristics.

After trying a variety of mathematical models classically used to represent the blended properties of a system, weighted average models were found to best fit the data. These models predict the mixture response by a weighted average or linear interpolation between the response of two pure chemicals on either an arithmetic or a logarithmic scale. This "weighted average" model is readily extendable to three or more compounds. A summary of the response data and the precision of these two models is given in Table 1-1. Neither the arithmetic nor logarithmic scale model shows any clear advantage when applied over the entire data set. However, the logarithmic model gives much poorer estimates than the arithmetic model in some cases. Both models are able to predict mixture response to within about ±30 percent of the observed value, which is about as good as the single chemical data on which the models are based. There is some advantage to the logarithmic scale model in that it has a discrete solution, while the arithmetic scale model must be solved iteratively or graphically.

TABLE 1-1. COMPARISON OF PERCENT ERROR FOR ARITHMETIC AND LOGARITHMIC WEIGHTED AVERAGE MODELS FOR MIXTURES

	Average Percent Error of Model Prediction			
	OVA		TLV	
Compound Mixtures	Arithmetic	Logarithmic	Arithmetic	Logarithmic
Acetic Acid and Chloroform	25	20	-83	-88
Acetic Acid and Cyclohexane	31	11	4	-37
Acetic Acid and Acetone	33	27	-3	-28
Acetone and Chloroform	39	17	-21	-80
Acetone and Cyclohexane	31	28	7	3
Benzene and Methyl Ethyl Ketone	-9	19	9	9
Benzene and Methanol	-1	-121	10	8
Chloroform and Cyclohexane	29	-5	-13	-90
Methanol and Methyl Ethyl Ketone	-16	-87	12	9
Benzene, Methanol, and Methyl Ethyl Ketone	-9	-50	12	9

Compound	Response Factor*		Compound	Response Factor*	
	OVA	TLV		OVA	TLV
Acetic Acid	1.64	15.60	Cyclohexane	0.47	0.70
Acetone	0.80	1.22	Methanol	4.39	2.01
Benzene	0.29	1.07	Methyl Ethyl Ketone	0.64	1.12
Chloroform	9.28	**			

*Ratio of Actual Concentration to Instrument Response at 10,000 ppmv Response (DuBose and Harris, 1981)

**A 10,000 ppmv response to Chloroform with TLV is not achievable.

SECTION 2

COMPUTATION METHODS

This section describes and discusses methods for estimating concentrations when VOC instrument responses are known. The fractional composition of the detected vapors must also be known. Computed and graphical estimates are discussed.

In general, the VOC instrument response to a mixture of compounds is intermediate to the individual responses to each one of them at the same total concentration. This effect may be approximated by a weighted average of the responses (or linear interpolation in the case of two chemicals). An estimate of the weighted average response is

$$R_A = \sum_i p_i a_i C_T^{b_i} e^{\frac{1}{2}s_i^2} \qquad (1)$$

where

R_A = the estimated weighted average response,
p_i = the fraction of the mixture total concentration accounted for by compound i ($p_i = C_i/C_T$),
a_i = exp(A) with "A" from Brown, et al (1980) for component i,
b_i = coefficient "B" from Brown, et al (1980) for component i,
s_i = parameters "SE" from Brown, et al (1980) for component i,
C_T = $\sum C_i$, the total concentration, and
C_i = the concentration in the mixture of compound i.

The coefficients A, B, and SE can be found in Tables 5-169 and 5-170 of Brown, et al (1980) for selected compounds.

The above discussion involves the prediction of an instrument response when the actual concentration of mixture components are known. In a practical situation, the reverse is the case: the response is observed and it is desired to estimate the concentration of the constituents. Basically, this cannot be done without some additional information. The compound identification of the constituents must be known. If the constituent proportions are also known, the total concentration can be computed assuming the above model is correct. The total concentration (C_T) is estimated by solving equation 1.

Equation 1 cannot be solved explicitly for total concentration. An iterative solution is required. This can be done using the Newton-Rhapson method. Let

$$f(C_T) = \sum_I p_i a_i C_T^{b_i} e^{\frac{1}{2} s_i^2} - R$$

where R is the observed instrument response, and

$$f'(C_T) = \sum_I p_i b_i a_i C_T^{b_i - 1} e^{\frac{1}{2} s_i^2}.$$

Then the iteration formula is

$$C_{j+1} = C_j - f(C_j)/f'(C_j).$$

A reasonable starting value C_o is R, the observed instrument response.

Alternatively, a weighted logarithmic average may be used. In this case

$$\log (R_L) = \sum_I p_i \left[\log a_i + \tfrac{1}{2} s_i^2 + b_i \log C_T\right] \qquad (2)$$

where R_L is the estimated instrument response using a weighted logarithmic average and logarithms are to base e.

In contrast to the previously given weighted arithmetic average model (equation 1), this weighted logarithmic average model (equation 2) has an explicit solution for actual total concentration:

$$\log C_T = \frac{\log R - \sum p_i \left(\log a_i + \tfrac{1}{2} s_i^2\right)}{\sum p_i b_i}$$

For binary mixtures the solutions are as follows. The arithmetic weighted average iteration formula is

$$C_{j+1} = C_j - f(C_j)/f'(C_j)$$

where

$$f(C_T) = p_1 a_1 C_T^{b_1} e^{\frac{1}{2} s_1^2} + p_2 a_2 C_T^{b_2} e^{\frac{1}{2} s_2^2} - R,$$

$$f'(C_T) = p_1 b_1 a_1 C_T^{b_1-1} e^{\frac{1}{2} s_1} + p_2 b_2 a_2 C_T^{b_2-1} e^{\frac{1}{2} s_2^2},$$

and

$$C_o = R \text{ or another suitable starting value.}$$

The logarithmic weighted average solution is

$$\log C_T = \frac{\log R - p_1 \left(\log a_1 + \tfrac{1}{2} s_1^2\right) - p_2 \left(\log a_2 + \tfrac{1}{2} s_2^2\right)}{p_1 b_1 + p_2 b_2}$$

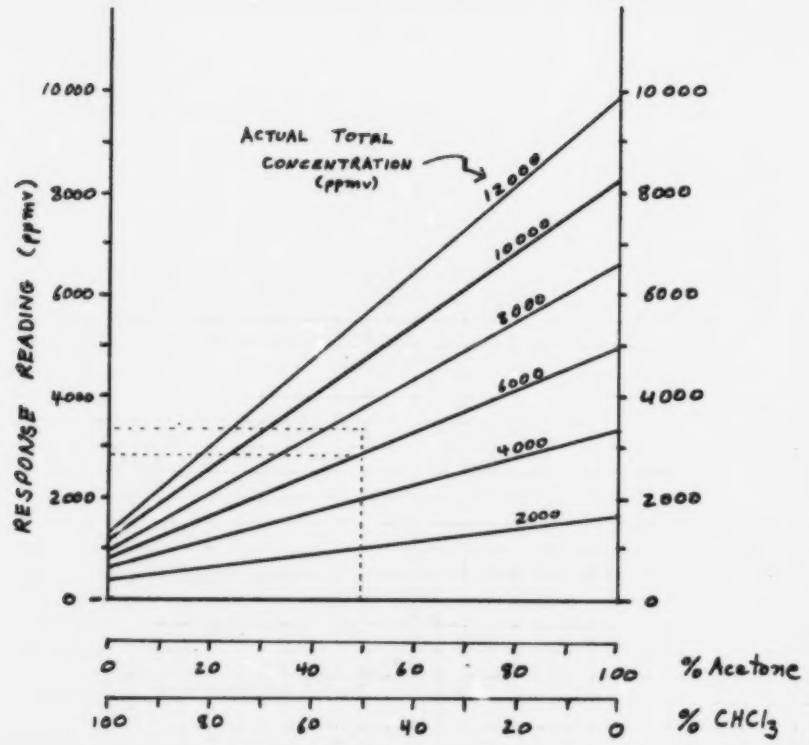
A simpler solution for multiple cases of a binary mixture is the construction of a nomograph. A nomograph similar to Figure 3-11 or 3-23 of Section 3 can be quickly prepared on a sheet of ordinary or semi-log graph paper. Select a sequence of total concentrations C_T in the expected range. Values of A, B, and SE are given in Tables 5-169 and 5-170 of Brown, et al (1980). Using these values, compute

$$R = \exp\ (A + B \cdot \log C_T + \tfrac{1}{2}SE^2)$$

at each selected concentration for both compounds in the binary mixture.

The horizontal axis of the nomograph should represent percent compositions; the vertical axis should be instrument response. Plot the pair of predicted responses R for each selected concentration at the appropriate compositions. Connect the two points with a straight line.

An example nomograph for TLV readings on acetone and chloroform appears in Figure 2-1 with the corresponding summary calculations. Figure 2-1 should be compared to Figure 3-19 of Section 3. To read the nomograph, use the response and composition to find the concentration. Consider a binary mixture of acetone and chloroform at equal concentrations and a TLV response of 2800 ppmv. The point at 50 percent acetone and 2800 ppmv response falls on the line marked for 6000 ppmv total concentration in Figure 2-1. Thus, the concentration of acetone is estimated at 50 percent of 6000 ppmv. This case is from Table 3-3 of Section 3. The actual response reading was 3375 ppmv at actual concentration of acetone and chloroform of approximately 2900 ppmv. Figure 2-1 gives an estimated total concentration of 7000 at 50 percent acetone and a reading of 3375 ppmv. Therefore, the estimated concentration of acetone is 50 percent of 7000 ppmv, which compares to the actual concentration 2900 ppmv for an error of 21 percent.



CHLOROFORM

$a = 1.1337$
$b = 0.637191$
$S_e = 0.267978$

$$R = e^{a} C^{b} e^{\frac{1}{2}S_e^2}$$

ACETONE

$a = -0.22007$
$b = 0.991616$
$S_e = 0.452099$

C	R
2000	409
4000	836
6000	823
8000	788
10000	1140
12000	1280

C	R
2000	1668
4000	3316
6000	4758
8000	6594
10000	8228
12000	9858

Figure 2-1. Example Nomograph for Mixtures of Acetone and Chloroform

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SECTION 3

DISCUSSION AND RESULTS

Two types of portable hydrocarbon detectors were used in this study: the J. W. Bacharach "TLV Sniffer" and the Century Systems "OVA-108". Although the detection methods differ between the two devices, their practical use is similar. The instrument draws in a sample through a probe and displays a concentration, by volume, of the sample. This instrument response depends not only on the concentration of the gas being read, but also on the calibration gas and its concentration.

A previous report (G. E. Brown, et al., 1980) found an empirical model that fitted the relationship between instrument response (R) and actual concentration (c) of gas in air reasonably well:

$$R = a \cdot c^{b}$$

The coefficients a and b are dependent on instrument type, the gas being detected, and also the calibration gas. These coefficients and related values were given for 168 chemicals for the two instrument types used in this report. Methane was used for calibration. Response factors (F), where

$$F = \frac{\text{Actual Concentration}}{\text{Instrument Response}},$$

were also estimated at 10,000 ppmv actual concentration. A second report (DuBose and Harris, 1981) presented response factors at 10,000 ppmv instrument response.

Most practical applications of hydrocarbon detectors are not concerned with pure chemical compounds in air. This raises the question about instrument responses to mixtures. A small pilot test involving mixtures of Benzene, Methanol, and Methyl Ethyl Ketone was initially done. Figures 3-1 through 3-3 show the points that were tested (some extreme points are not shown). Additionally, several ternary mixtures were prepared and tested.

A tentative additive model was examined:

$$R_M = R_1 + R_2$$

where R_M = instrument response to mixture, and
R_i = response to instrument to concentration C_i of chemical i alone.

The predictions from this model tended to be lower than the observed results. The reason for this becomes apparent if one considers a case where both gases are the same. Unless the coefficient b=1 in equation 1, the effects will not be additive for increments of the same gas. In general, $b \neq 1$ for the compounds tested. The behavior of a mixture cannot be expected to be simpler than that of a pure compound.

Several empirical approaches to model the instrument response to compound mixtures were examined for this report. These included, among others, classical mixture polynomial models,

$$R = A_1C_1 + A_2C_2 + A_{12}C_1C_2,$$

exponential type models,

$$R = a(C_1 + C_2)^b e^{d_1C_1 + d_2C_2}$$

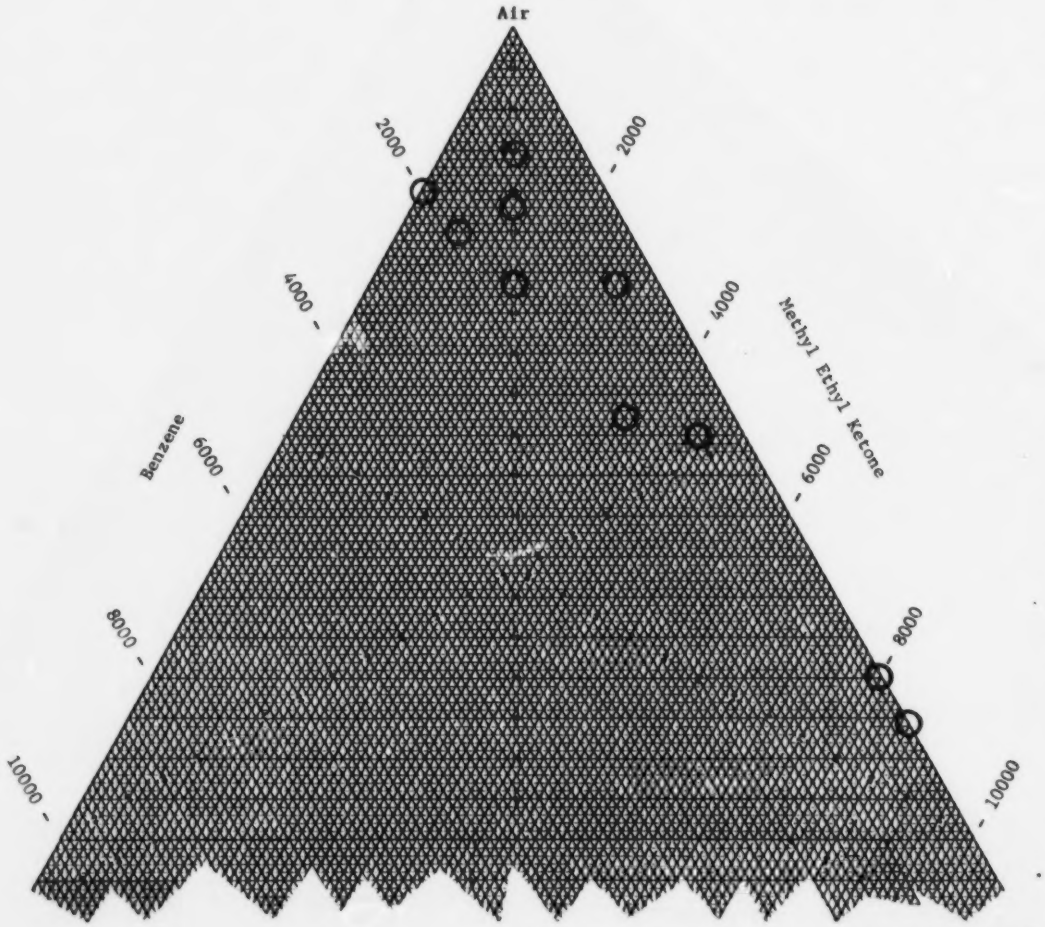

Figure 3-1. Experimental Points Tested with Mixtures of Benzene and Methyl Ethyl Ketone in Pilot Study

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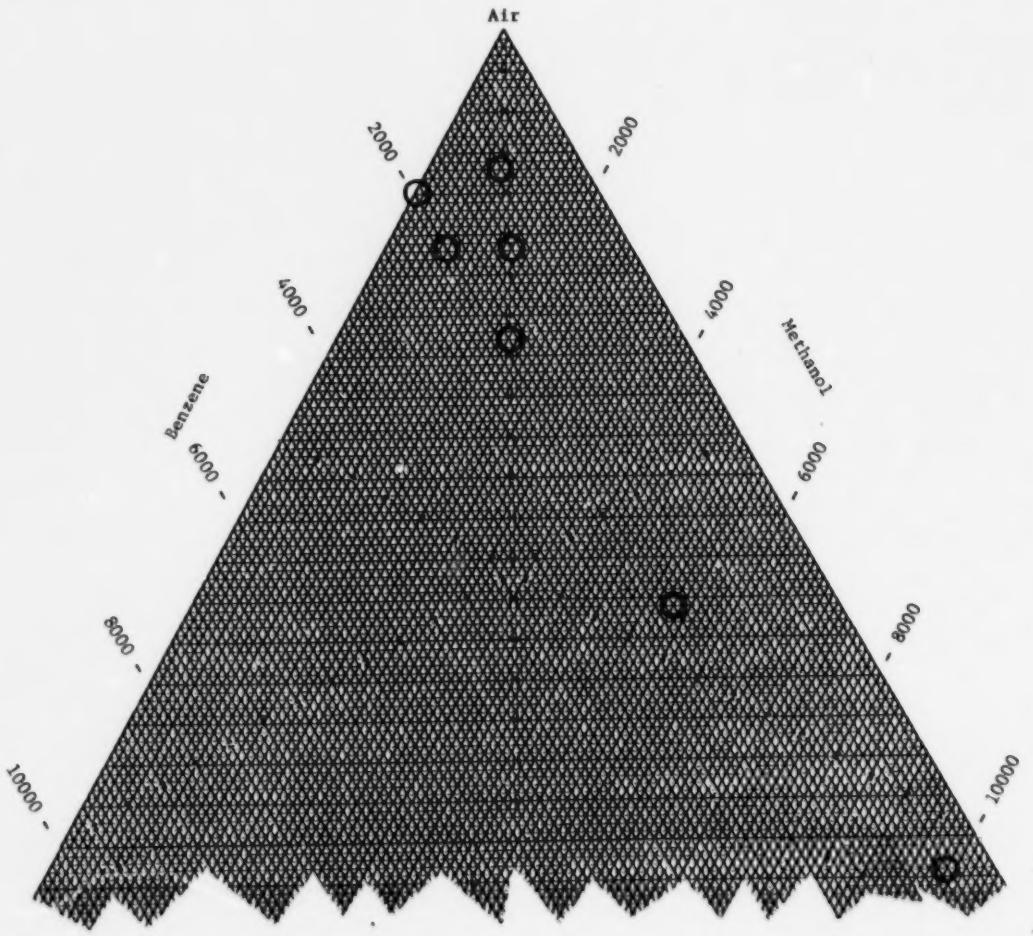


Figure 3-2. Experimental Points Tested with Mixtures of Benzene and Methanol in Pilot Study

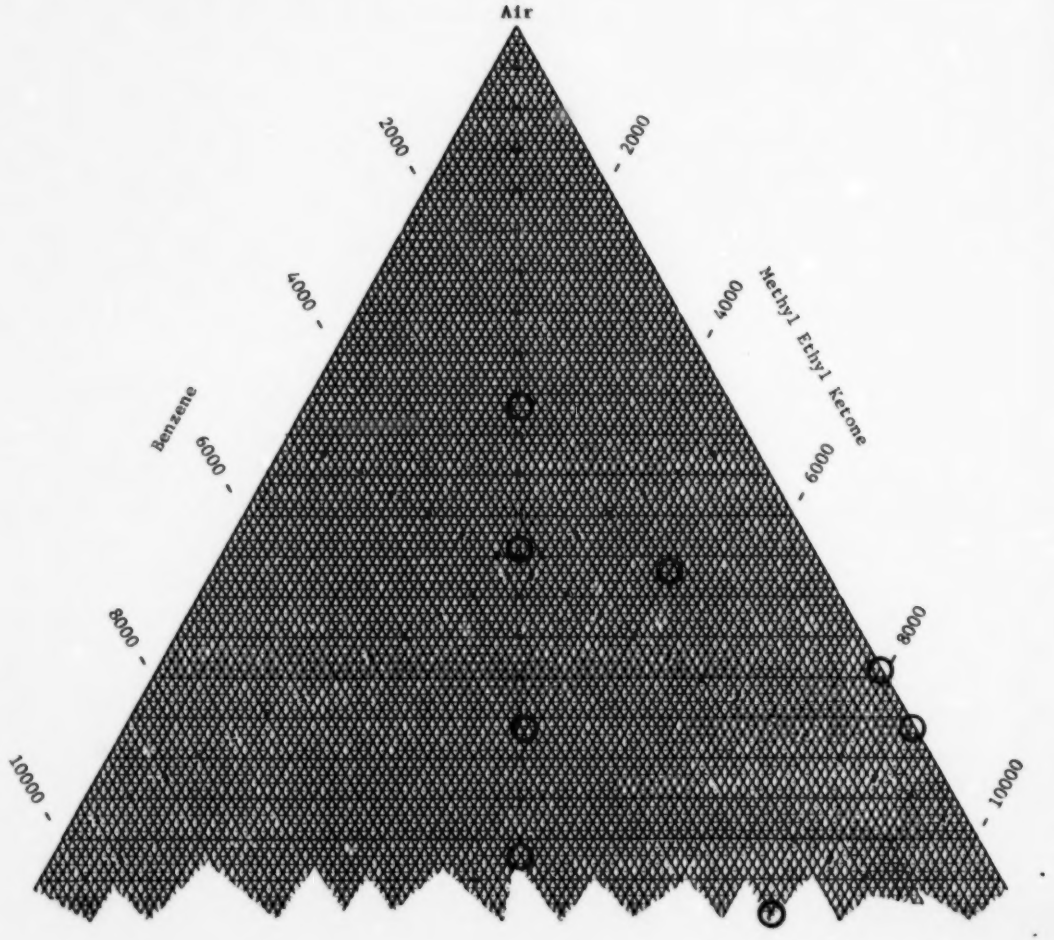


Figure 3-3. Experimental Points Tested with Mixtures of Methanol and Methyl Ethyl Ketone in Pilot Study

where C_i = concentration of ith compound, and

A_1, A_2, A_{12}, a, b, d_1, and d_2 are coefficients to be evaluated.

The most desirable models would be ones based on the response characteristics of pure compounds. Various interpolation or weighted average models were therefore also examined. One of these interpolation models appeared to offer the best fit.

Consider a two component mixture with a total concentration C_T. That is, let

$$C_T = C_1 + C_2$$

where C_i is the concentration of gas i and C_T is constant. Thus,

$$C_2 = C_T - C_1$$

and the instrument response to this gas mixture may be viewed as a function of the concentration C_1 alone. More simply, the response is a function of the percent of gas i in the fixed total C_T.

Figure 3-4 illustrates how this function might behave. A discontinuous response is not expected. A synergistic response is possible. Both of these cases would indicate that instrument response to mixtures is complex. If such complexity is dominant, then it is doubtful that any approximate model could be based on the responses to the pure compounds alone.

A natural hypothesis is that the response to a mixture will be intermediate to the responses of the pure compounds. The simplest conception of this model is a weighted average (or linear interpolation in the case of two compounds). Reanalysis of the OVA data for benzene, methanol, and methyl ethyl ketone supported this model.

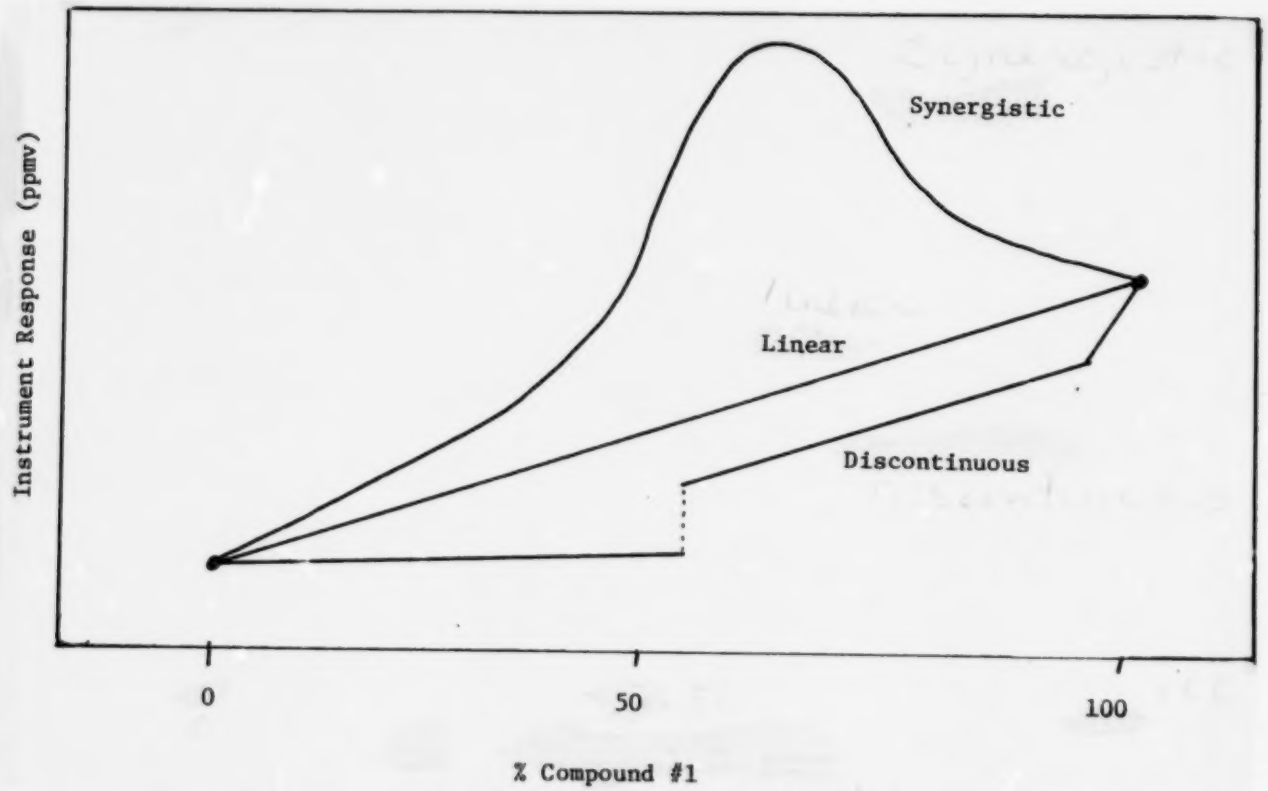


Figure 3-4. Possible Relationships for Instrument Response and Percent Composition in a Binary Mixture

Consequently, an experiment was designed to verify the interpolation model. Four chemical compounds were chosen: acetic acid, acetone, cyclohexane, and chloroform. These compounds were chosen to represent a variety of responses in the pure state and for mutual nonreactivity. For each pair, at least two feasible total concentrations (C_T) were chosen. One or more mixtures in air were prepared at each of these total concentrations. Additionally, pure preparations of both compounds were tested at the selected concentrations. The latter serve both as experimental points and as a quality control check. Figures 3-5 through 3-10 give the points that were tested.

Figures 3-11 through 3-16 summarize the results. These figures display the instrument response as a function of percent of total concentration for one of the two compounds in the mixture. The interconnecting lines serve only to link the data points taken at the same nominal concentration and should not be interpreted as representing intermediate values.

The nominal concentrations are the intended experimental concentrations. In actuality these vary somewhat from the actual experimental concentration due to various errors of measurement. In most cases, however, they are accurate enough to draw basic conclusions from the graphs.

The general hypothesized model predicted that the instrument response to mixtures would be intermediate to the response to corresponding pure compound concentrations. The results here verify this to be the case for the seven compounds tested. The particular hypothesized model predicted that the intermediate responses would fall on a straight line when plotted against the component concentrations or component percent of total concentration. The data show no strong evidence that this is not the case (except Figure 3-14 for TLV). However, the graphs for the OVA instrument indicate a possible curvature.

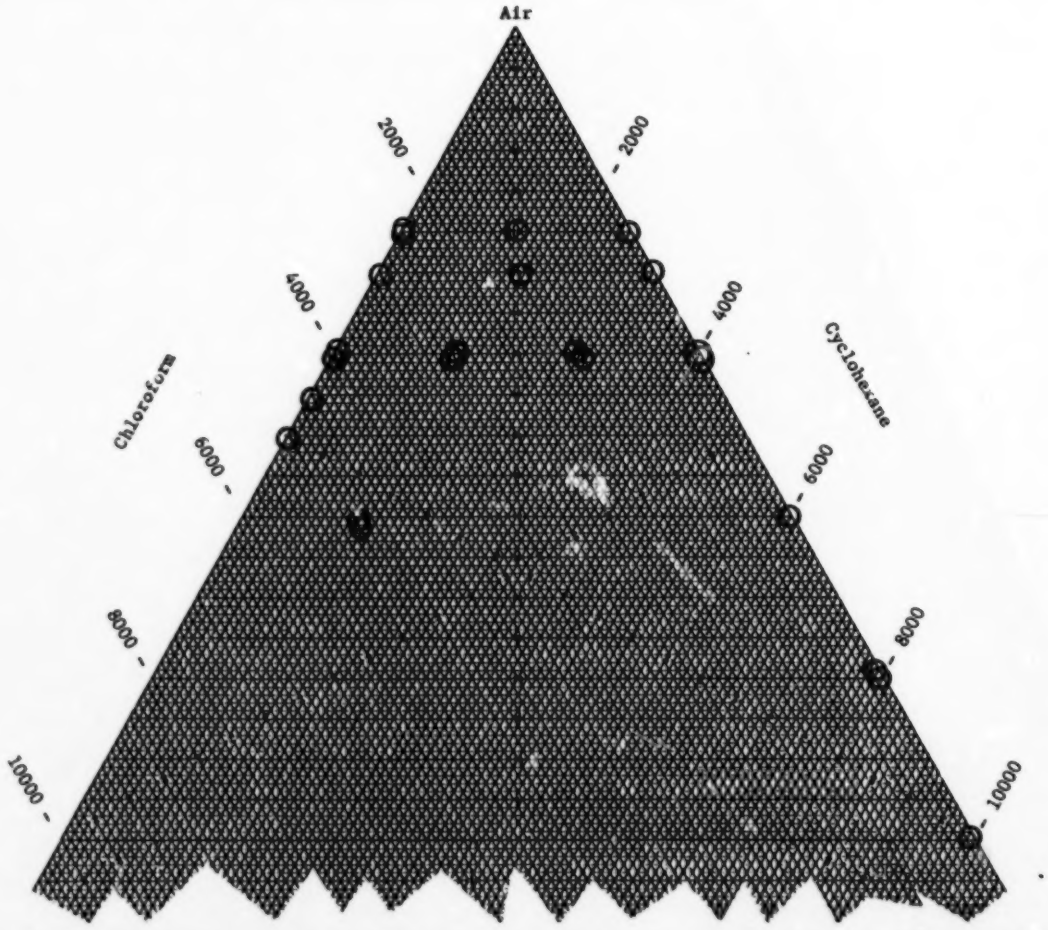


Figure 3-5. Experimental Points Tested With Mixtures of Chloroform and Cyclohexane

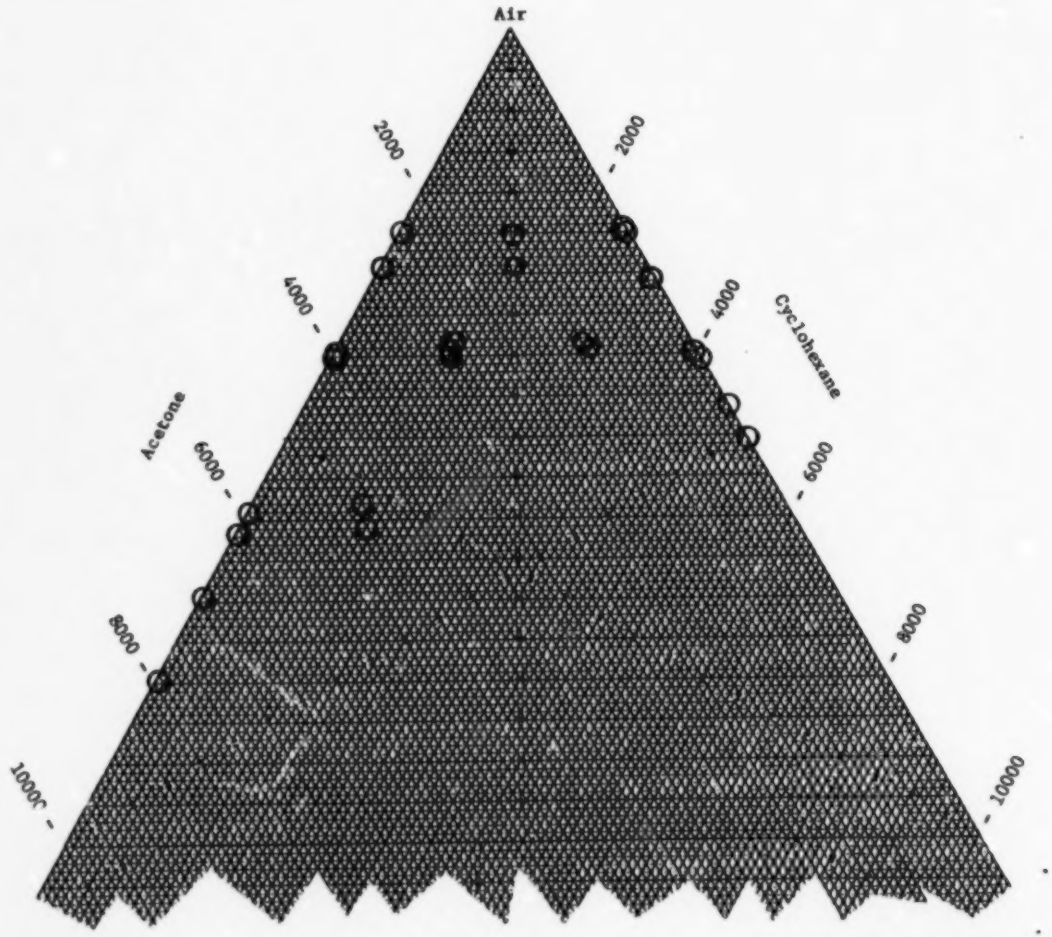


Figure 3-6. Experimental Points Tested With Mixtures of Acetone and Cyclohexane

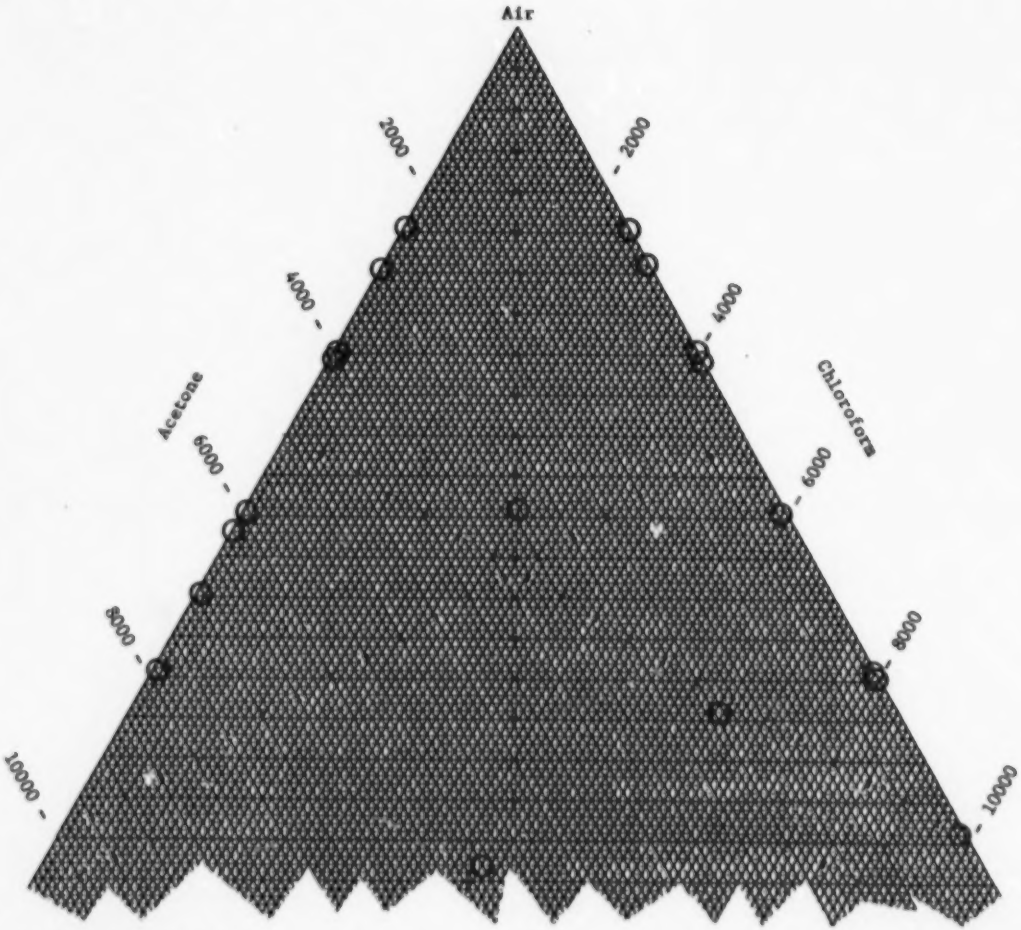


Figure 3-7. Experimental Points Tested With Mixtures of Acetone and Chloroform

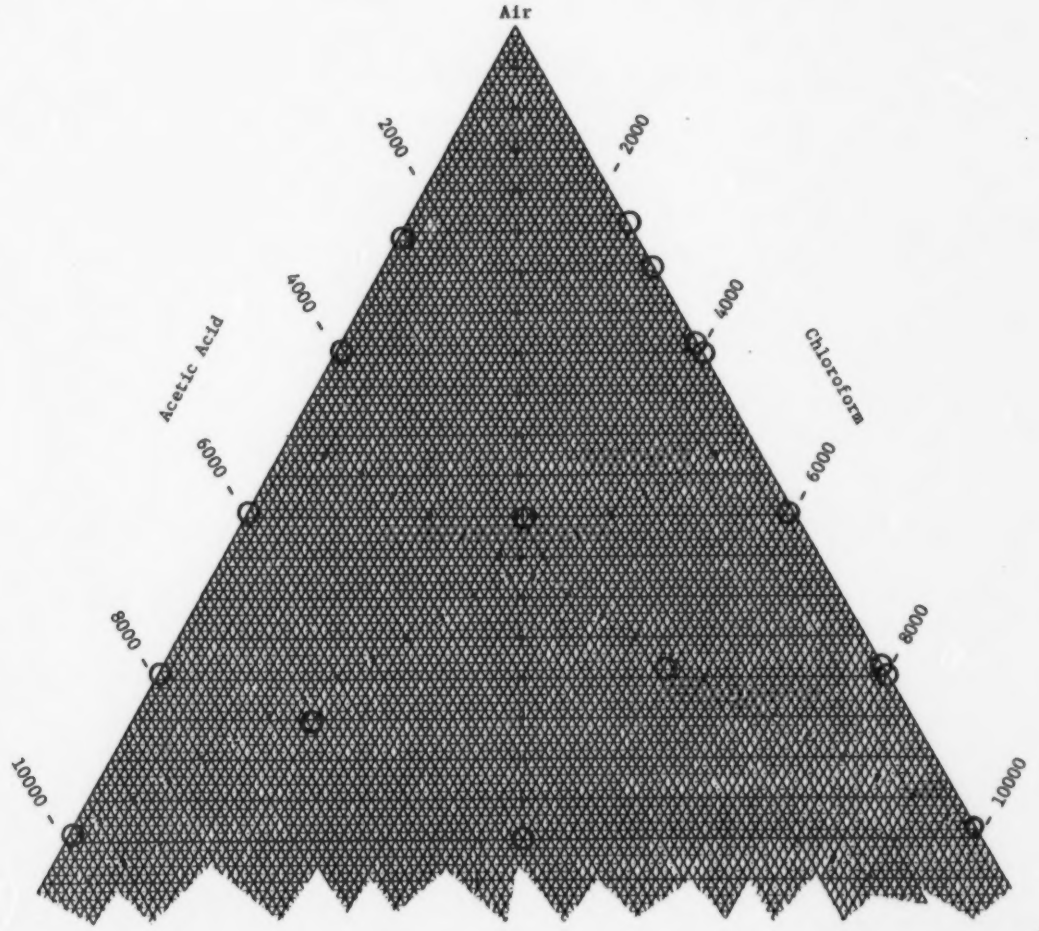


Figure 3-8. Experimental Points Tested With Mixtures of Acetic Acid and Chloroform

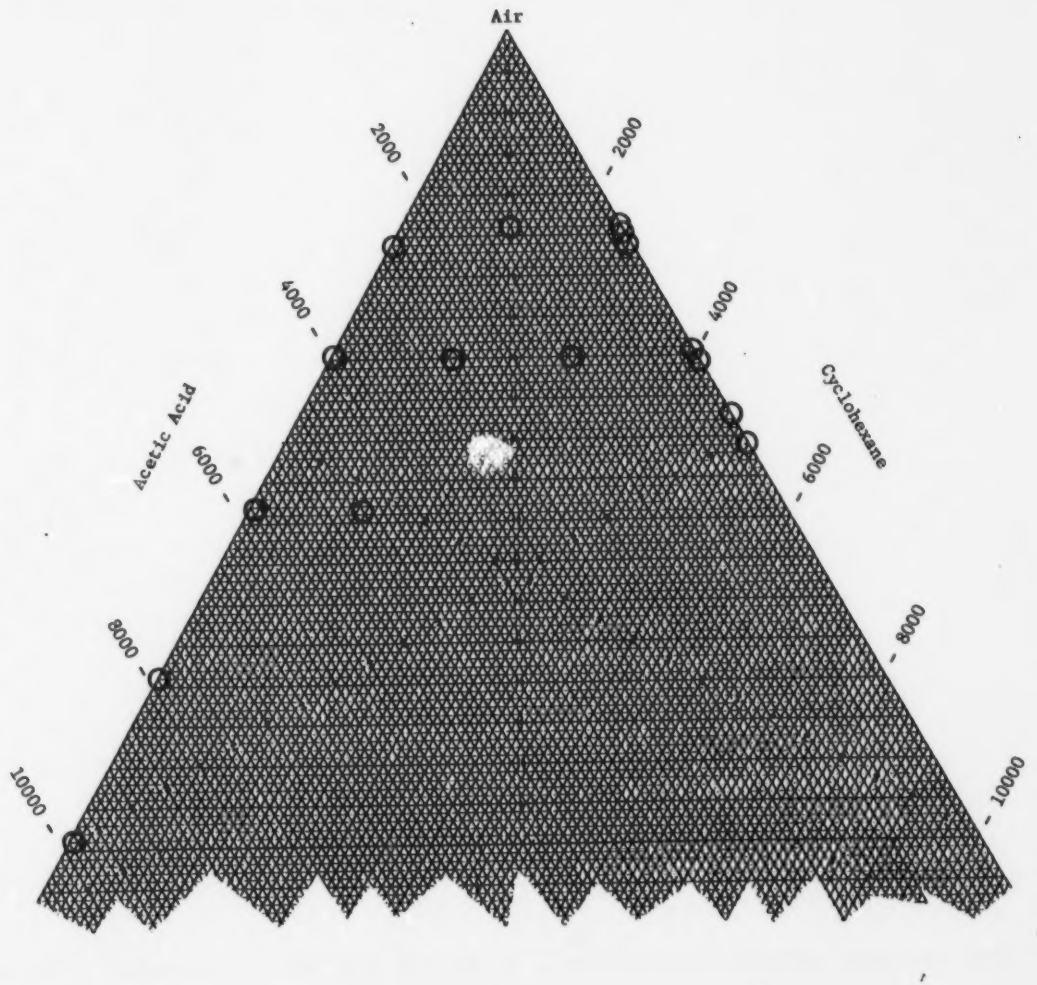


Figure 3-9. Experimental Points Tested With Mixtures of Acetic Acid and Cyclohexane

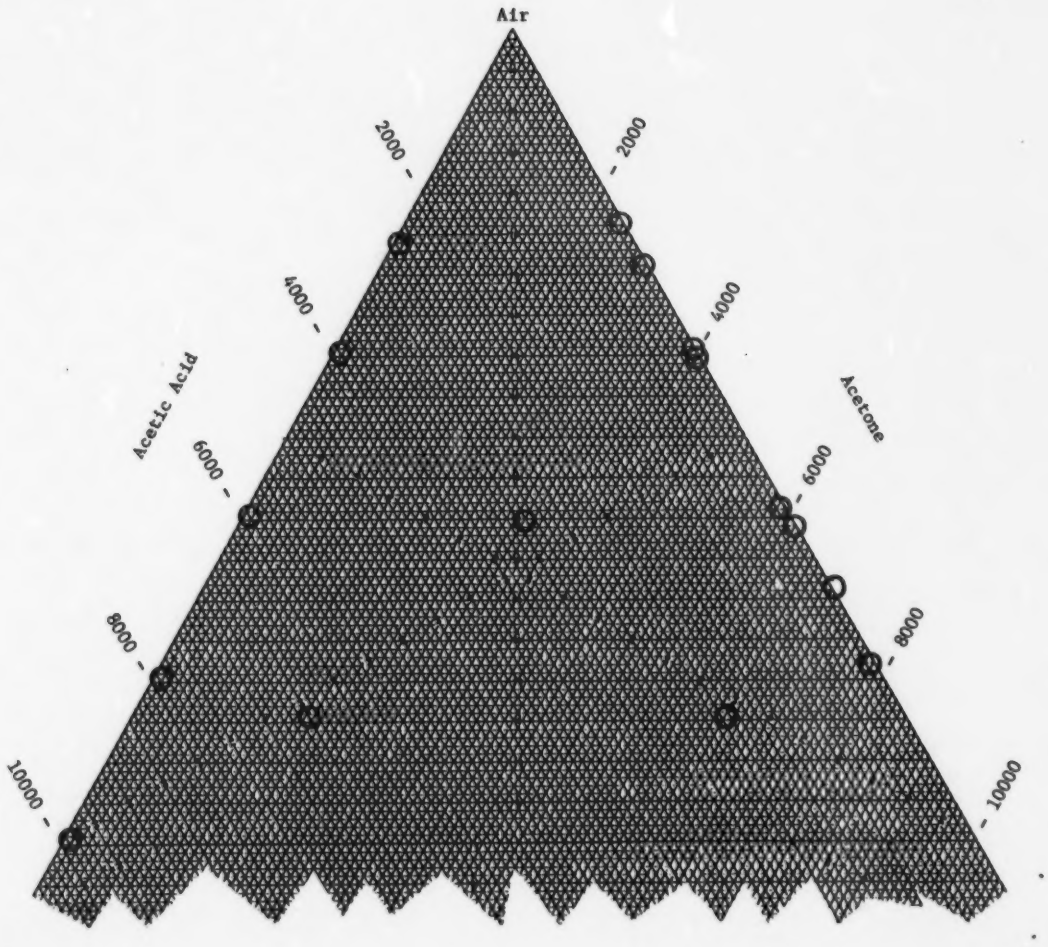
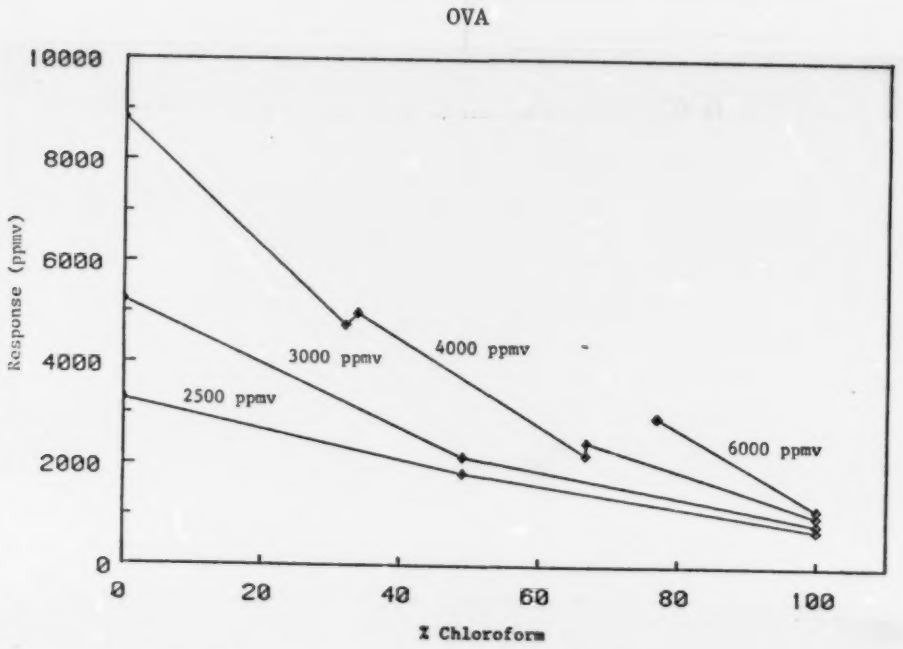


Figure 3-10. Experimental Points Tested With Mixtures of Acetic Acid and Acetone



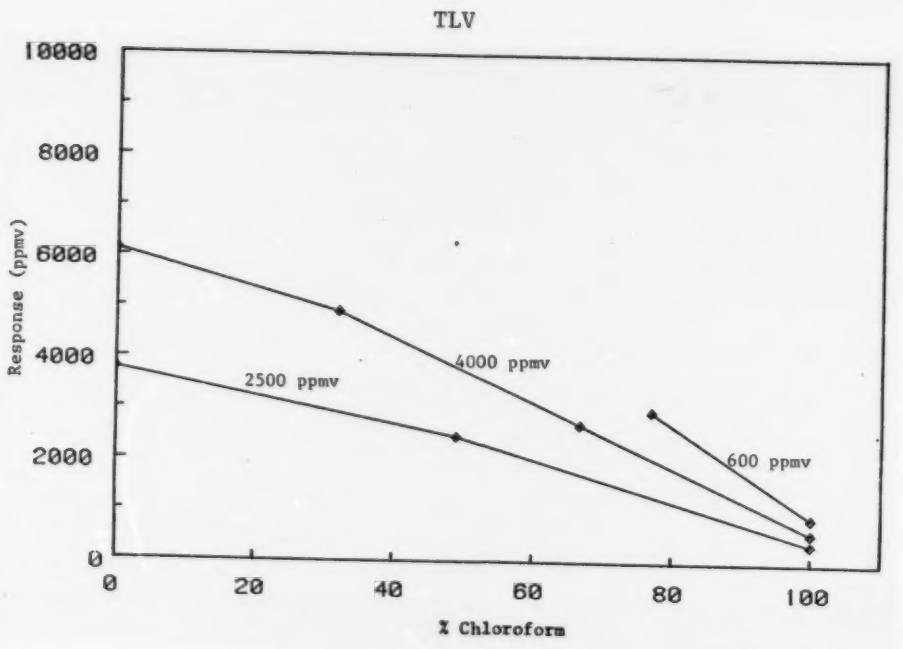


Figure 3-11. Instrument Response to Mixtures of Chloroform and Cyclohexane

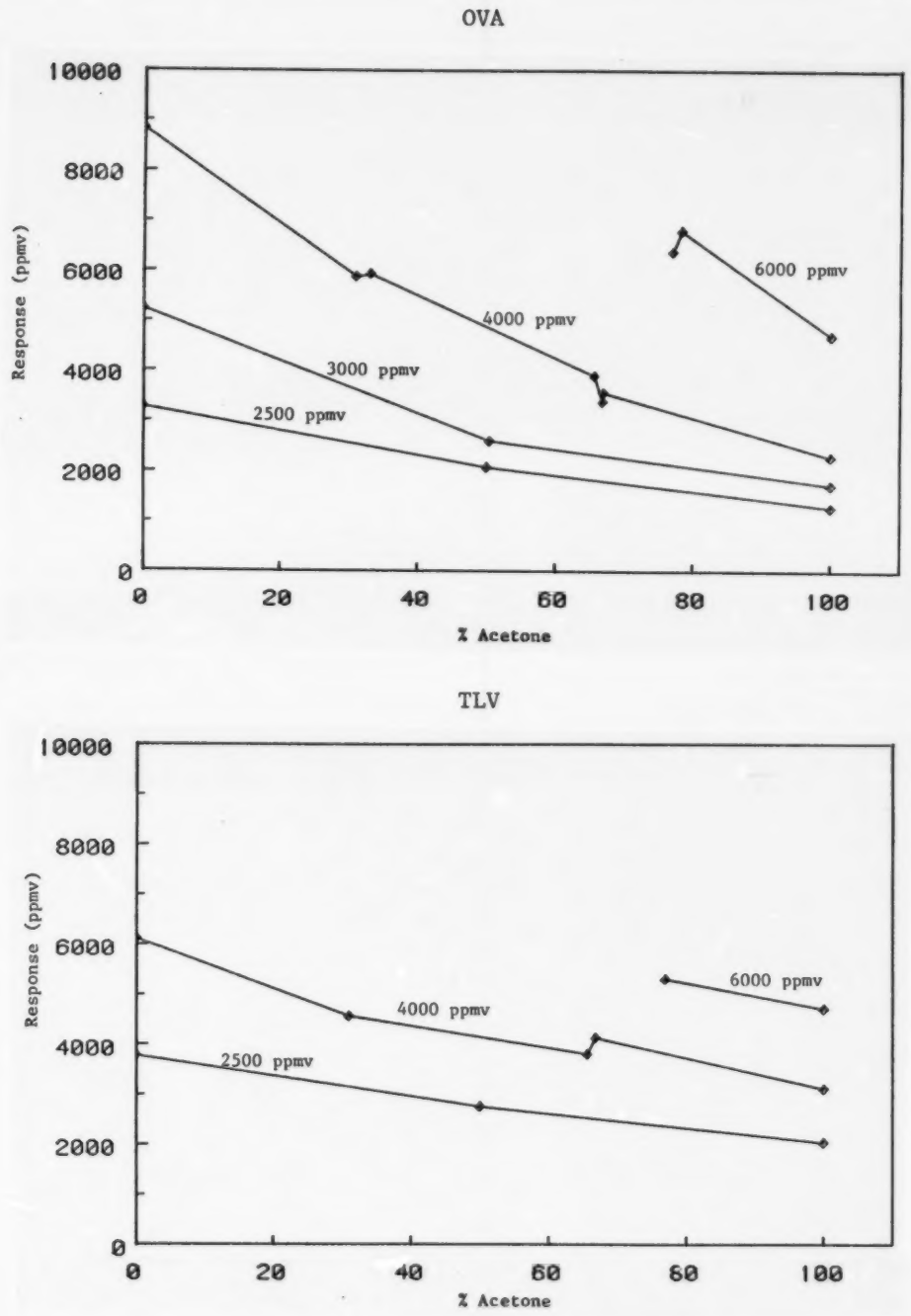


Figure 3-12. Instrument Response to Mixtures of Acetone and Cyclohexane

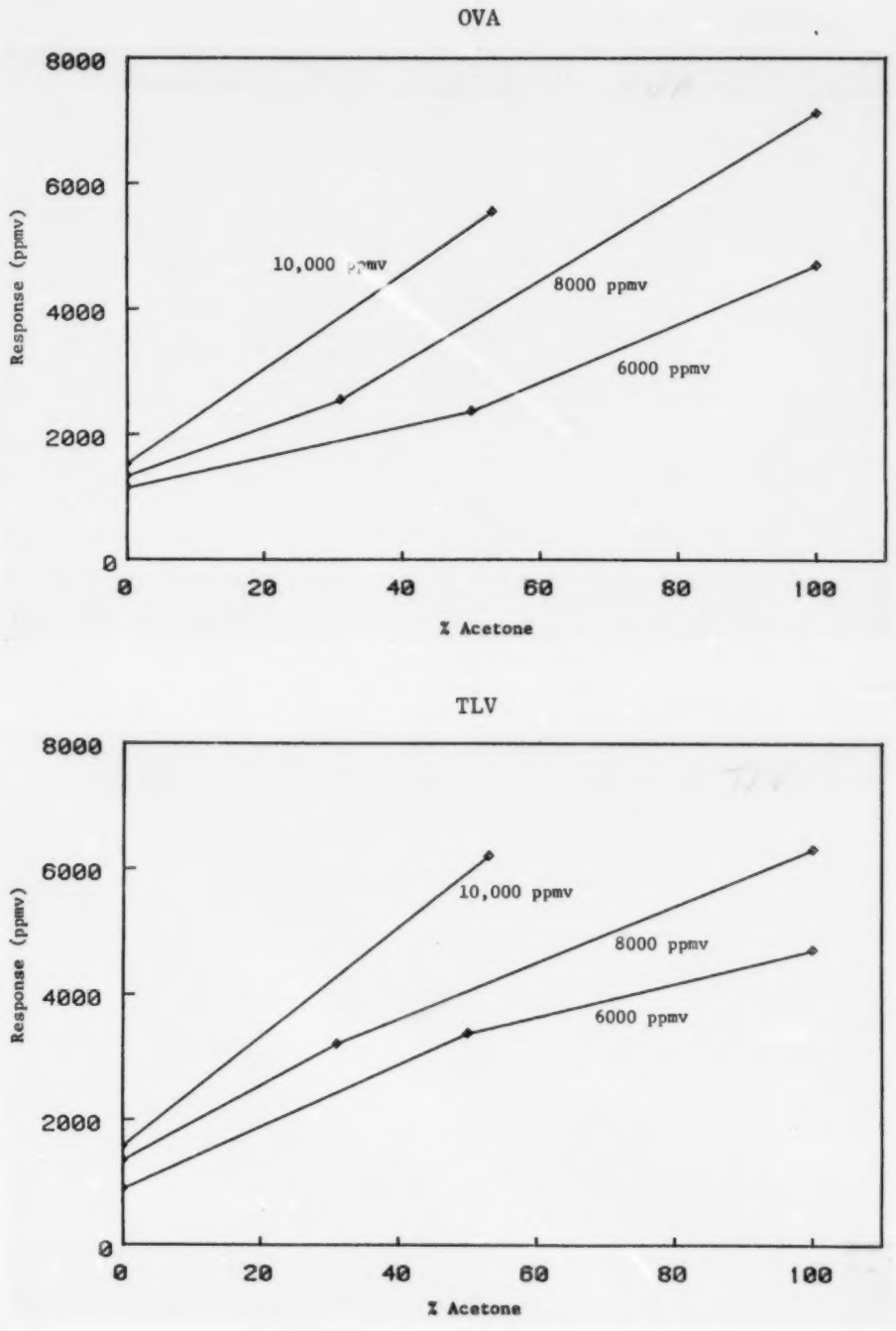


Figure 3-13. Instrument Response to Mixtures of Acetone and Chloroform

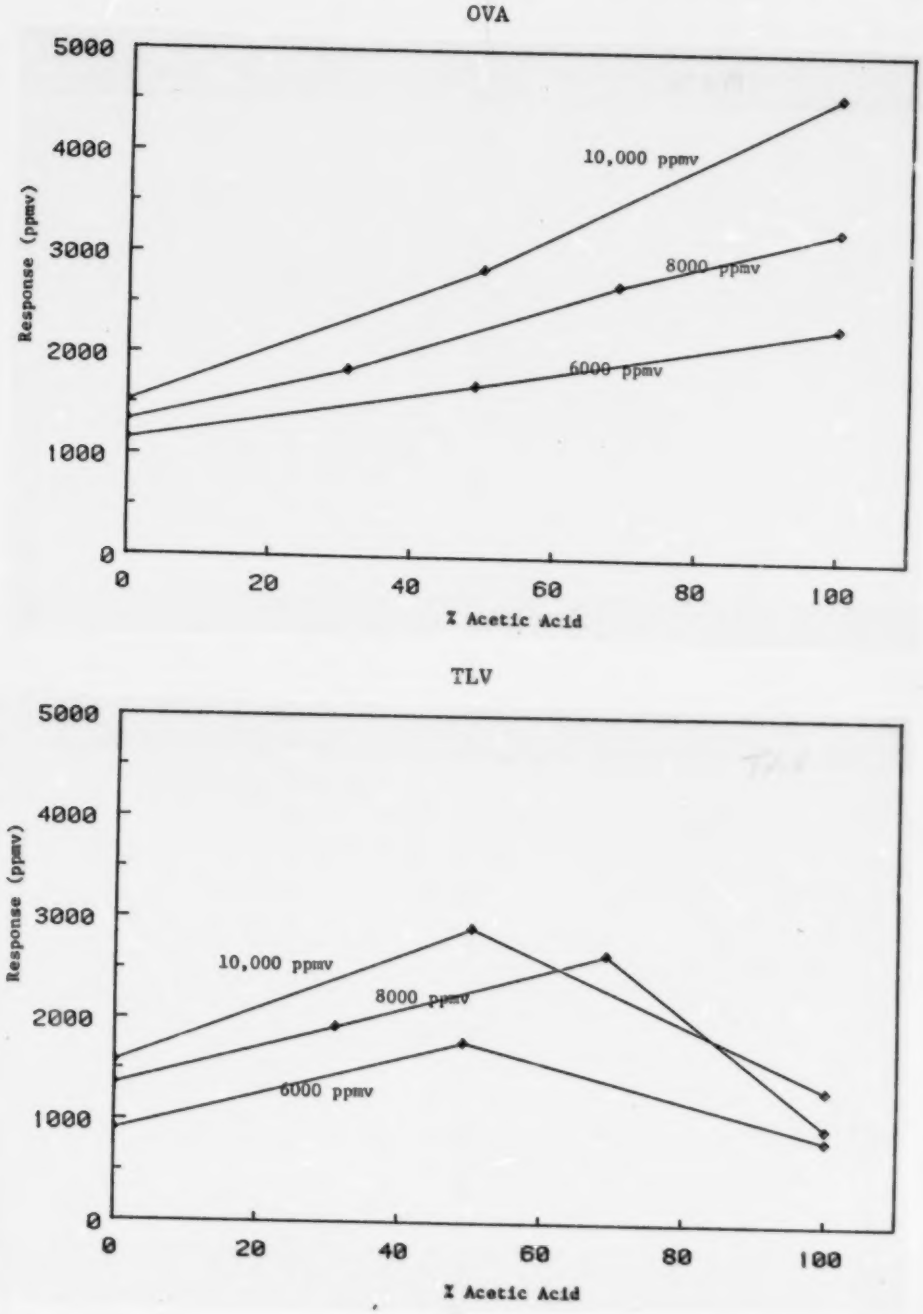


Figure 3-14. Instrument Response to Mixtures of Chloroform and Acetic Acid

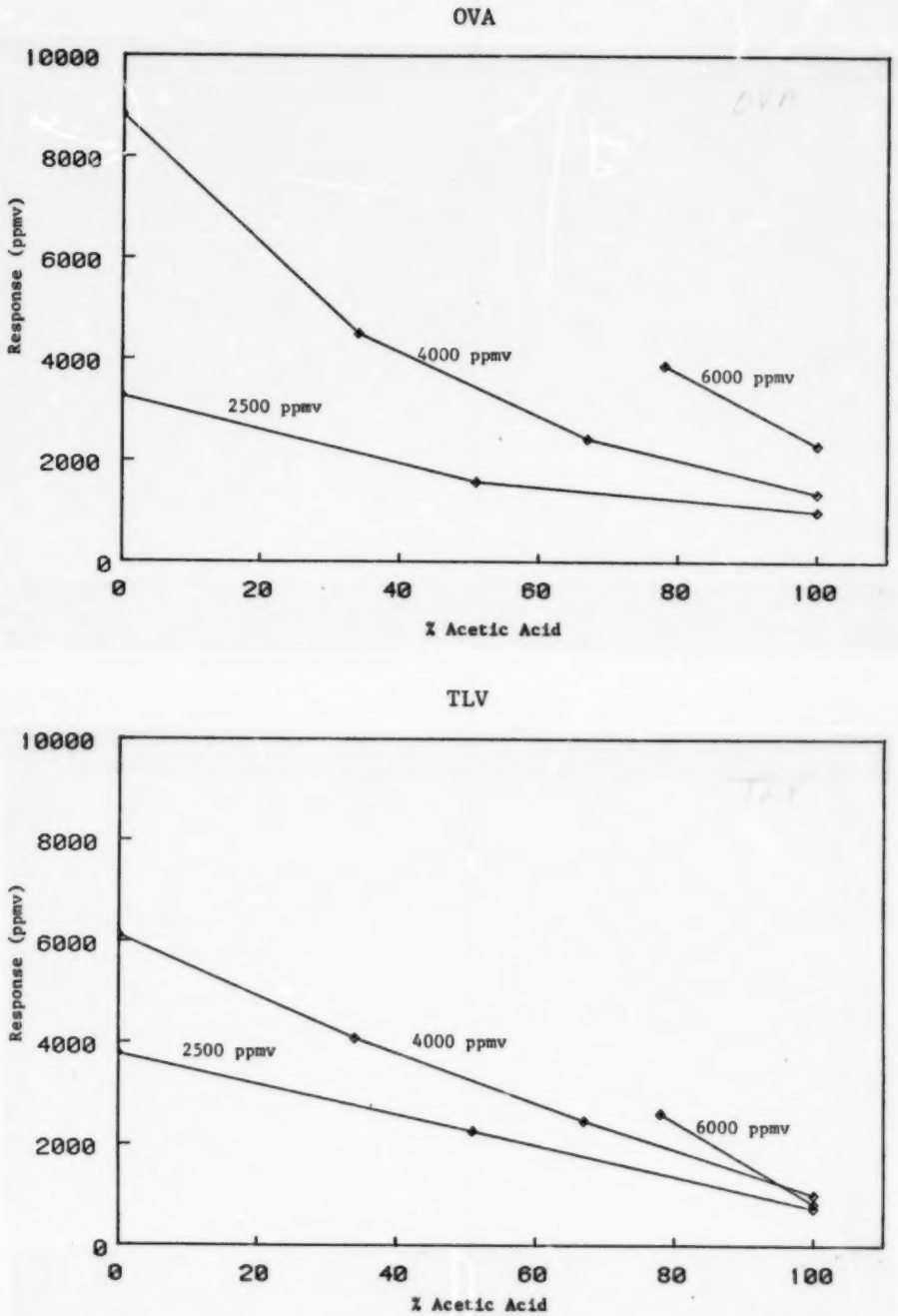


Figure 3-15. Instrument Response to Mixtures of Acetic Acid and Cyclohexane

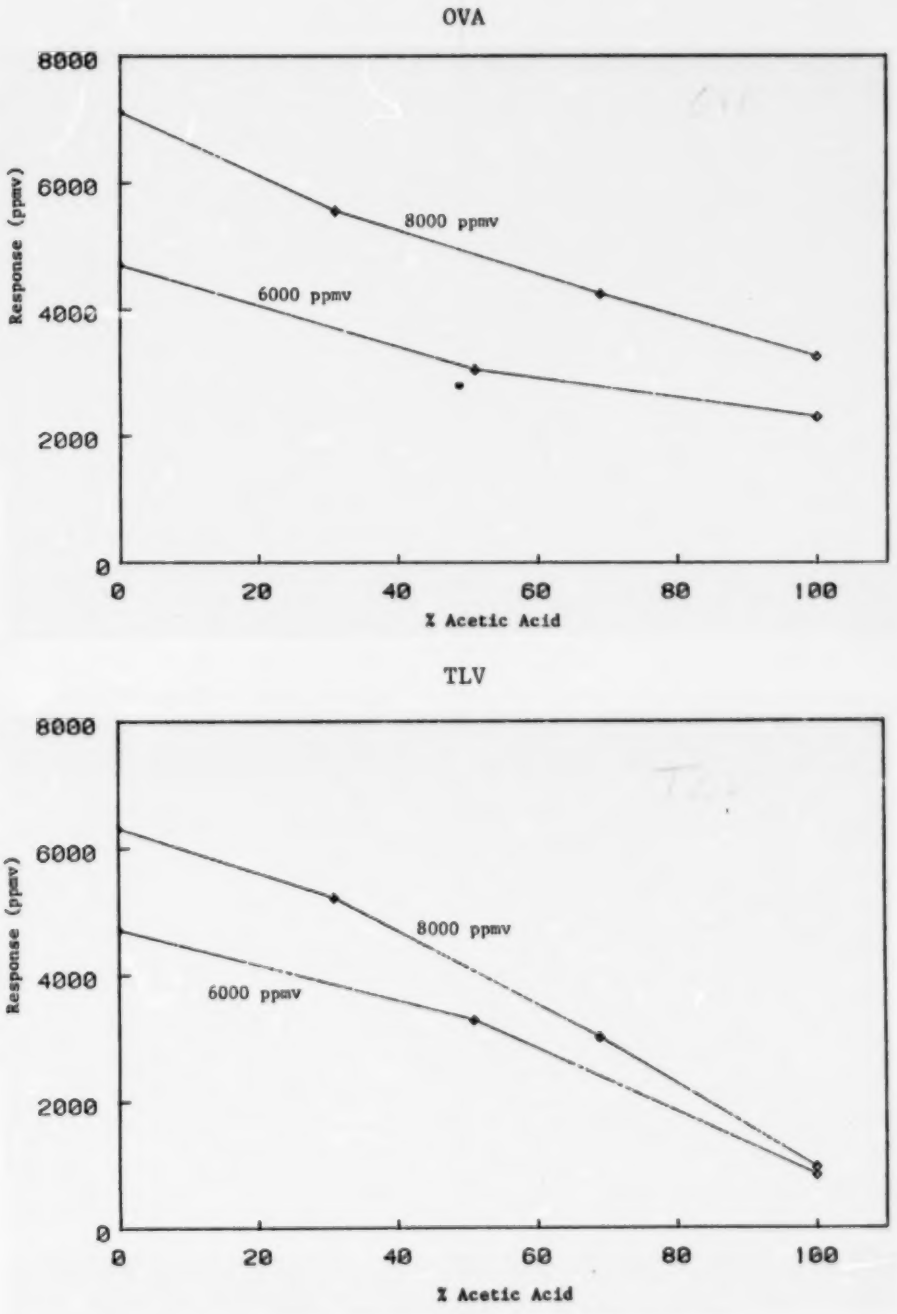


Figure 3-16. Instrument Response to Mixtures of Acetic Acid and Acetone

The empirical model used for pure compounds is an exponential one:

$$R = aC_1^b$$

In fact, this equation was fitted to the pure compound data in its logarithmic form (Brown, et al, 1980):

$$\log R = \log a + b \cdot \log C.$$

A mechanism to handle the apparent curvature for the OVA in Figures 3-11 through 3-16 is an alternative logarithmic scale model. That is, the logarithm of the instrument response to a mixture may be predicted by linear interpolation between the logarithms of the responses to the pure compounds at the same total concentration. Figure 3-17 presents the OVA responses on a logarithmic scale for chloroform and cyclohexane. Comparing this figure to Figure 3-11 supports the hypothesis of linearity in the logarithmic scale for the OVA. The result is similar for OVA responses to other mixtures. This is not consistent with the pilot study mixture results for OVA.

Tables 3-1 through 3-6 gives the mixture response data and compare the arithmetic and logarithmic interpolation models. Tables 3-7 through 3-9 give similar information for the earlier benzene, methanol, and methyl ethyl ketone data. These tables show the compound concentrations for mixtures along with instrument responses, model predictions, and model percent errors. Both the arithmetic scale interpolation model and the logarithmic scale interpolation model results are given for both OVA and TLV.

The precision of the mixture response predictions must be interpreted in the light of achievable instrument precision. Both the OVA and TLV can repeatedly read a constant source within ±20 to ±30 percent of mean reading most (95%) of the time. Different OVA instruments can read the same source within 40 percent of mean reading most of the time. Different TLV instruments have about the same consistency as OVA's above 5000 ppmv response but

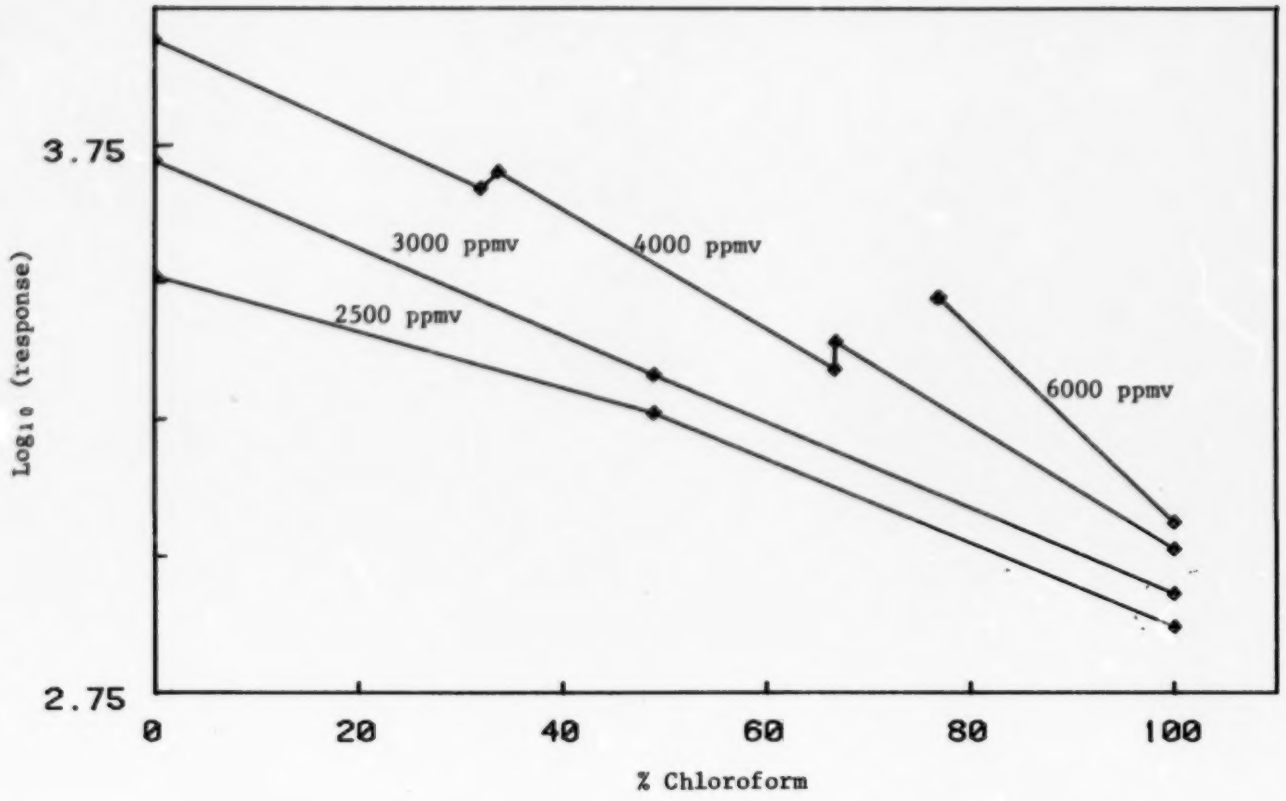


Figure 3-17. OVA Instrument Response on a Logarithmic Scale for Mixtures of Chloroform and Cyclohexane Showing Better Linearity than an Arithmetic Scale

TABLE 3-1. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF CHLOROFORM AND CYCLOHEXANE

Chloroform (ppmv)	Cyclohexane (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	% Error	Logarithmic Interpolation Prediction (ppmv)	% Error
			OVA			
1224	1262	1822	2620	30	1967	7
1300	2762	4745	6041	21	4496	-6
1330	2614	4980	5699	13	4210	-18
1480	1547	2148	3356	36	2414	11
2625	1310	2197	3448	36	2245	2
2635	1307	2448	3446	29	2243	-9
4642	1385	2945	4459	34	2623	-12
4658	1403	2948	4510	35	2646	-11
		$\sqrt{MSE}$ =	1204		351	
		Avg. % Error =	29		-4.5	
			TLV			
1224	1262	2450	2185	-12	1366	-79
1300	2762	4900	4325	-13	2954	-66
2625	1310	2700	2378	-14	1324	-104
4642	1385	2975	2640	-13	1419	-110
		$\sqrt{MSE}$ =	393		1523	
		Avg. % Error =	-13		-90	

TABLE 3-2. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF ACETONE AND CYCLOHEXANE

Acetone (ppmv)	Cyclohexane (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
1217	2715	5870	6946	15	6757	13
1254	1249	2070	3628	43	3555	42
1305	2623	5922	6862	14	6667	11
1480	1454	2588	4401	41	4293	40
2539	1333	3895	5709	32	5527	30
2618	1300	3383	5751	41	5567	39
2666	1319	3555	5864	39	5674	37
4577	1277	6786	8548	21	8223	17
4697	1409	6370	9061	30	8692	27
		$\sqrt{MSE}$ =	1895		1694	
		Avg. % Error =	31		28	
			TLV			
1217	2715	4550	5068	10	4899	7
1254	1249	2750	2977	8	2839	3
2539	1333	3800	4100	7	3934	3
2618	1300	4125	4115	<1	3951	-4
4697	1409	5300	5918	10	5740	8
		$\sqrt{MSE}$ =	398		272	
		Avg. % Error =	7		3.4	

TABLE 3-3. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF ACETONE AND CHLOROFORM

Acetone (ppmv)	Chloroform (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
2464	5488	2545	4390	42	3186	20
2910	2934	2372	4337	45	3323	29
5391	4758	5547	7872	30	5680	2
		$\sqrt{MSE}$ =	2055		667	
		Avg. % Error =	39		17	
			TLV			
2464	5488	3200	2711	-18	1772	-81
2910	2934	3375	2811	-20	1969	-71
5391	4758	6200	4975	-25	3297	-88
		$\sqrt{MSE}$ =	828		2037	
		Avg. % Error =	-21		-80	

TABLE 3-4. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF ACETIC ACID AND CHLOROFORM

Acetic Acid (ppmv)	Chloroform (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
2479	5483	1845	2604	29	2433	24
2946	3052	1695	2240	24	2139	21
4969	4981	2845	3820	26	3471	18
5540	2483	2695	3472	22	3281	18
		$\sqrt{MSE}$ =		779		565
		Avg. % Error =		25		20
			TLV			
2479	5483	1925	1151	-67	1127	-71
2946	3052	1775	1042	-70	1018	-74
4969	4981	2900	1441	-101	1409	-106
5540	2483	2650	1360	-95	1334	-99
		$\sqrt{MSE}$ =		1110		1136
		Avg. % Error =		-83		-88

TABLE 3-5. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF ACETIC ACID AND CYCLOHEXANE

Acetic Acid (ppmv)	Cyclohexane (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	% Error	Logarithmic Interpolation Prediction (ppmv)	% Error
			OVA			
1164	1135	1570	2375	34	1857	15
1371	2606	4495	5904	24	4785	6
2651	1332	2420	3884	38	2943	18
4643	1293	3870	5259	26	4053	5
		$\sqrt{MSE}$ =	1295		344	
		Avg. % Error =	31		11	
			TLV			
1164	1135	2250	2117	-6	1556	-45
1371	2606	4075	4230	4	3189	-28
2651	1332	2450	2640	7	1789	-37
4643	1293	2600	2859	9	1914	-36
		$\sqrt{MSE}$ =	190		737	
		Avg. % Error =	3.5		-37	

TABLE 3-6. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF ACETIC ACID AND ACETONE

Acetic Acid (ppmv)	Acetone (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
2465	5498	5545	8124	32	7560	27
3084	2933	3047	5093	40	4593	34
5431	2430	4235	5831	27	5331	21
		$\sqrt{MSE}$ =	2112		1597	
		Avg. % Error =	33		27	
			TLV			
2465	5498	5200	5002	-4	4172	-25
3084	2933	3275	3075	-7	2471	-33
5431	2430	3000	3044	1	2364	-27
		$\sqrt{MSE}$ =	164		838	
		Avg. % Error =	-3.3		-28	

TABLE 3-7. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF BENZENE AND METHYL ETHYL KETONE

Benzene (ppmv)	Methyl Ethyl Ketone (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
487	2694	5240	5189	-1	4799	-9
497	4469	9616	8458	-14	7990	-20
746	789	3042	2991	-2	2657	-14
1106	1104	5216	4803	-9	4272	-22
1169	3585	Off Scale	9687	-	8734	-
1594	1602	8867	7635	-16	6790	-31
1826	601	7416	6646	-12	6162	-20
		$\sqrt{MSE}$ =		778		1275
		Avg. % Error =		-9		19
			TLV			
487	2694	2775	2841	2	2839	2
497	4469	4075	4427	8	4425	8
746	789	1500	1435	-5	1431	-5
1106	1104	1850	2061	10	2057	10
1169	3585	3725	4291	13	4288	13
1594	1602	2575	2964	13	2960	13
1826	601	1825	2328	22	2325	22
		$\sqrt{MSE}$ =		358		356
		Avg. % Error =		9		9

TABLE 3-8. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF BENZENE AND METHANOL

Benzene (ppmv)	Methanol (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
487	9905	4115	4054	-1	2136	-93
500	19855	8166	6481	-26	4075	-100
869	838	2242	2701	17	1193	-88
988	11752	7066	7041	<1	2946	-140
1307	1340	4516	4550	1	1899	-138
1778	5333	7967	8554	7	2733	-191
1909	1929	7467	7296	-2	2958	-152
1974	681	6641	6663	<1	4057	-64
		$\sqrt{MSE}$ =	655		3535	
		Avg. % Error =	-0.5		-121	
			TLV			
487	9905	5225	5702	8	5654	8
500	19855	8400	10336	19	10282	18
869	838	1400	1395	<1	1358	-3
988	11752	5900	7024	16	6927	15
1307	1340	1975	2092	6	2030	3
1778	5333	4075	4611	12	4473	9
1909	1929	2725	2973	8	2878	5
1974	681	2150	2352	9	2303	7
		$\sqrt{MSE}$ =	840		790	
		Avg. % Error =	10		8	

TABLE 3-9. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF METHANOL AND METHYL ETHYL KETONE

Methanol (ppmv)	Methyl Ethyl Ketone (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
			OVA			
1676	4952	9767	8074	-21	5949	-64
2348	2353	3992	3774	-6	2308	-73
2694	8230	Off Scale	15235	-	11063	-
3206	3168	5592	5478	-2	3264	-71
4304	4352	9093	8091	-12	4721	-93
5067	5094	Off Scale	9853	-	5670	-
6740	6671	Off Scale	13831	-	7760	-
9779	3264	9990	7880	-27	4201	-138
15694	5261	Off Scale	14087	-	7140	-
19693	1496	8516	6826	-25	4648	-83
		$\sqrt{MSE}$ =	1368		3881	
		Avg. % Error =	-16		-87	
			TLV			
1676	4952	6800	5321	-28	5218	-30
2348	2353	3400	3417	1	3337	-2
2694	8230	8150	8780	7	8576	5
3206	3168	3975	4588	13	4464	11
4304	4352	5475	6198	12	6007	9
5067	5094	6050	7240	16	7002	14
6740	6671	8300	9470	12	9122	9
9779	3264	5275	7999	34	7759	32
15694	5261	9675	12539	23	12086	20
19693	1496	8150	11115	27	10961	26
		$\sqrt{MSE}$ =	1752		1571	
		Avg. % Error =	12		9	

can be less consistent below this level. The empirical models used to predict responses to pure compounds can be in error by 20-30 percent or more.

The model predictions are computed using coefficients given by Brown et al. (1980). The arithmetic scale interpolation model is as follows:

$$R_A = p_1 a_1 C_T^{b_1} e^{\frac{1}{2}s_1^2} + p_2 a_2 C_T^{b_2} e^{\frac{1}{2}s_2^2}$$

where R_A = predicted instrument response to the mixture

$C_T = C_1 + C_2$

C_i = concentration of compound i in the mixture

$p_i = C_i/C_T$

b_i = coefficient B from Brown, et al. (1980) for compound i

a_i = exp(A) from Brown, et al. (1980) for compound i

$e^{\frac{1}{2}s_i^2}$ = bias adjustment for linear scale using S_i = SE from Brown, et al. (1980) for compound i

The logarithmic scale interpolation model is as follows:

$$\log(R_L) = p_1[\log a_1 + b_1 \log C_T + \tfrac{1}{2}s_1^2] + p_2[\log a_2 + b_2 \log C_T + \tfrac{1}{2}s_2^2]$$

where R_L = predicted instrument response to the mixture, and log is the natural logarithm (base e) function.

The mean square error (MSE) is computed from:

$$MSE = \Sigma(\text{predicted} - \text{response})^2/(\text{number of cases}).$$

Both the arithmetic and logarithmic scale models may be extended to ternary and higher mixtures. The arithmetic weighted average is

$$R_L = \sum_i p_i \left[\log a_i + b_i \log C_T + \tfrac{1}{2} S_i^2\right]$$

and the logarithmic weighted average is

$$R_A = \sum_i p_i A_i C_T^{bi} e^{\frac{1}{2}s_i^2}$$

with a notation analogous to the above for the i^{th} compound.

Table 3-10 gives the experimental results and predictions for certain ternary mixtures of benzene, methanol, and methyl ethyl ketone. These mixtures were prepared as part of the pilot study.

TABLE 3-10. INSTRUMENT RESPONSES AND PREDICTIONS FOR MIXTURES OF BENZENE, METHANOL, AND METHYL ETHYL KETONE

Benzene (ppmv)	Methanol (ppmv)	Methyl Ethyl Ketone (ppmv)	Response (ppmv)	Arithmetic Interpolation Prediction (ppmv)	Arithmetic Interpolation % Error	Logarithmic Interpolation Prediction (ppmv)	Logarithmic Interpolation % Error
				OVA			
1216	1186	2410	9758	8398	-14	5249	-46
1385	2789	1397	9616	8151	-15	3586	-63
1597	824	800	6666	6751	1.3	4021	-40
1049	1087	1092	5717	5264	-8	2879	-50
			$\sqrt{MSE}$ =	1026		4235	
			Avg. % Error =	-9		-50	
				TLV			
1216	1186	2410	3600	3973	10	3897	8
1385	2769	1397	3750	4127	10	4002	7
1597	824	800	2400	2749	15	2694	12
1049	1087	1092	2325	2625	13	2567	10
			$\sqrt{MSE}$ =	351		272	
			Avg. % Error =	12		9	

SECTION 4

QUALITY ASSURANCE

The quality assurance procedures for the laboratory work consisted of four parts:

- Replicate instrument readings
- Replicate mixture preparations
- Instrument calibration verification
- Pure compound preparations for comparison with previous data

Each instrument was read twice in nearly all cases and sometimes three times if enough gas remained. The readings were taken roughly in random order among the instruments. The data values presented earlier are mean readings.

Some replicate mixture preparations were included. The repeatability in preparation of bagged gas mixtures and in instrument responses is apparent from their entries in Tables 3-1 and 3-2. The repeatability in responses is also visible in the corresponding Figures 3-11 and 3-12. The variation present is much smaller than the variation among different mixture levels.

The calibration of each instrument was verified at least twice each day of operation. Table 4-1 presents the verification log. Two standard methane gas preparations were used: 7990 ppmv and 490 ppmv in air.

TABLE 4-1. INSTRUMENT CALIBRATION VERIFICATION LOG

Date	Time	Methane Gas Concentration	OVA		TLV-7
			5797	5799	
3-23	1600	7990	8000	Not Used	Not Used
"	"	490	430	"	"
"	1700	7990	Off Scale	"	"
3-24	0855	7990	Off Scale	"	"
"	0907	7990	8000	"	"
"	0908	490	430	"	"
"	1103	7990	8000	"	"
"	1430	7990	8000	"	"
"	1610	7990	7500	"	"
3-25	1415	7990	8000	8000	8000
"	"	490	410	430	490
"	1710	7990	8100	8200	8050
3-26	0900	7900	8100	8100	7800
"	0910	7900	8000	8000	8200
"	"	490	405	410	490
"	1035	7990	8000	8000	8200
"	"	490	410	440	530
"	1430	7990	8000	8000	8200
"	1500	7990	8000	8100	8150
"	1630	7900	7900	8100	8150
"	"	490	400	450	580
3-27	0920	7990	8000	8000	8100
"	"	490	410	440	490
"	1120	7990	8000	8050	7950

Pure compound gas preparations were used to define the boundaries for mixtures (see Figures 3-11 through 3-16). These results can also be compared with previous data (Brown, et al., 1980). Figures 4-1 through 4-8 plot instrument response against actual concentration for both old and new data. Both scales are logarithmic so that the points tend to fall along a straight line. It can be readily seen that the new points associated with the mixture data generally fall in line with the previous points.

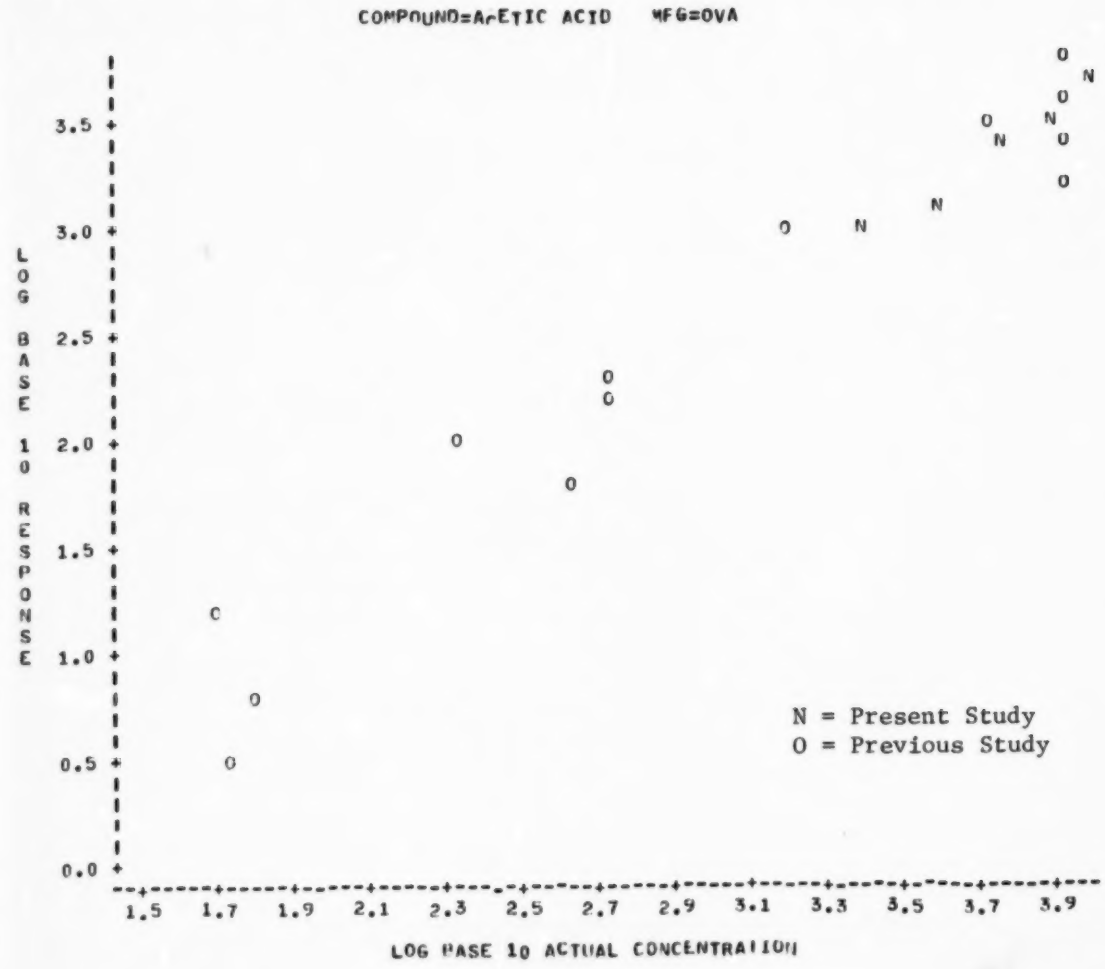


Figure 4-1. OVA Response to Acetic Acid

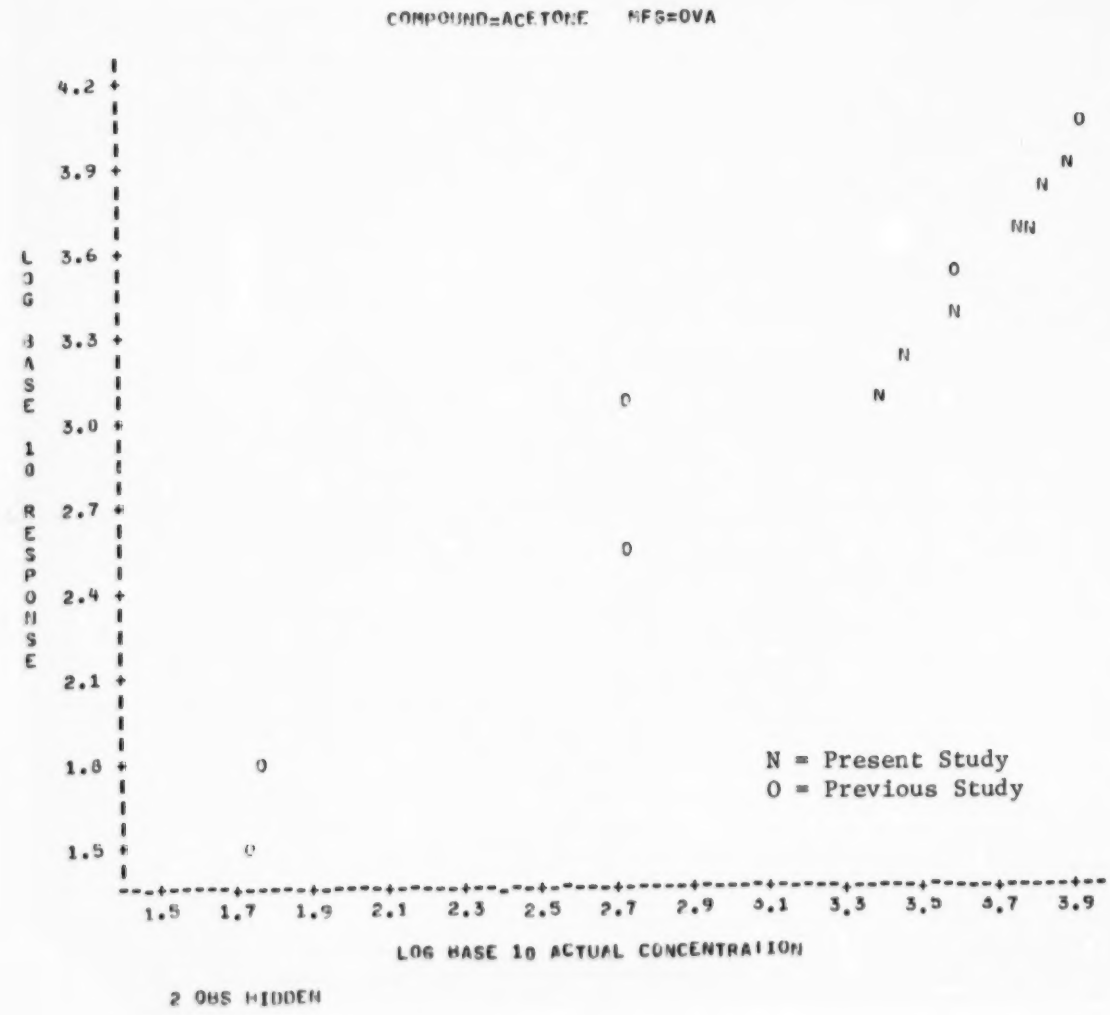


Figure 4-2. OVA Response to Acetone

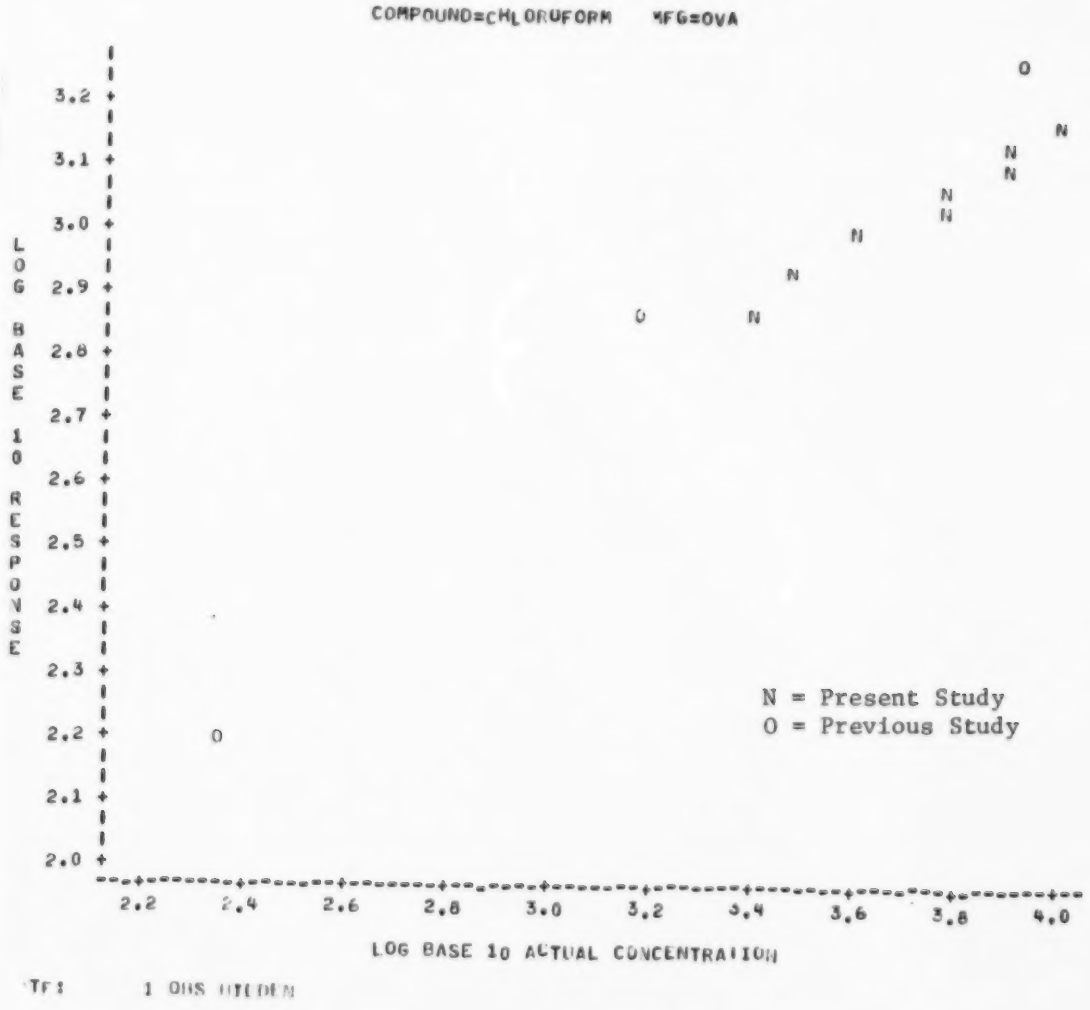


Figure 4-3. OVA Response to Chloroform

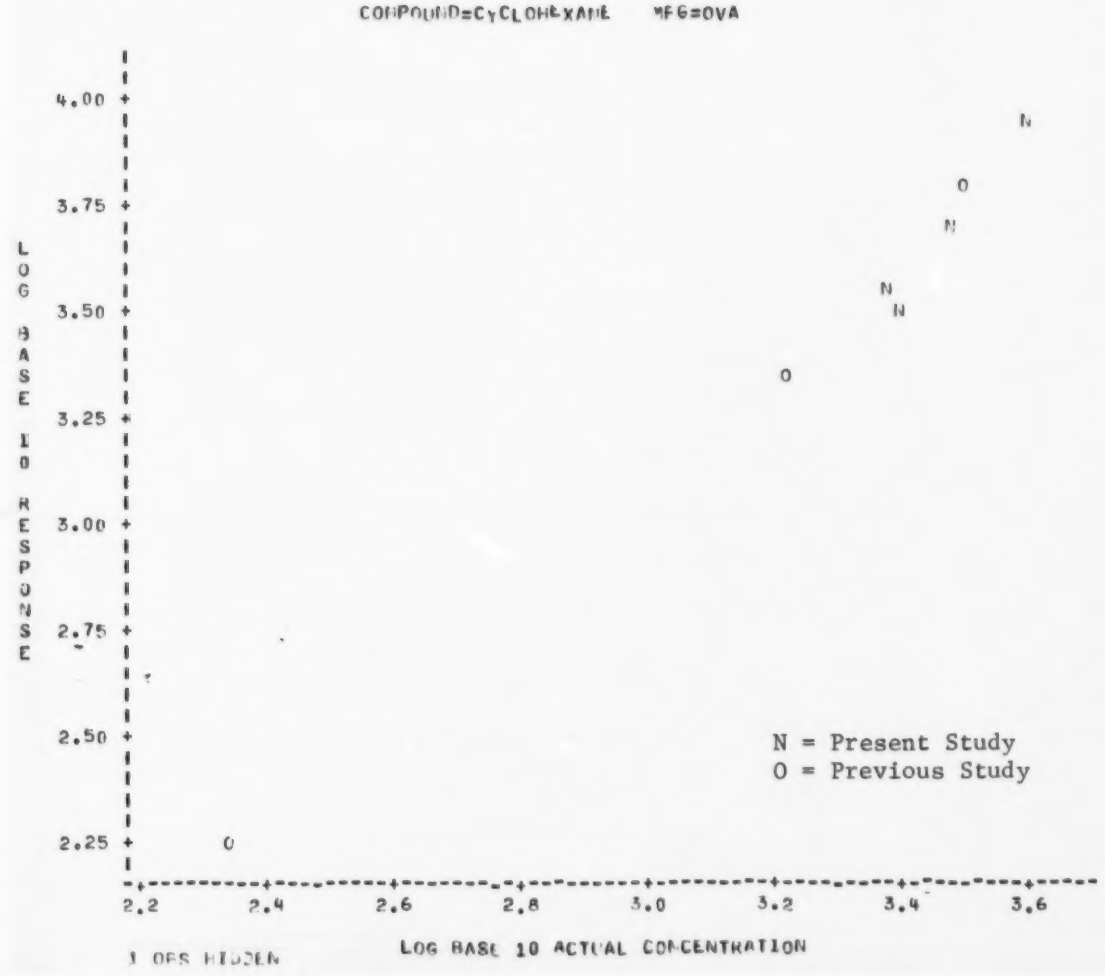


Figure 4-4. OVA Response to Cyclohexane

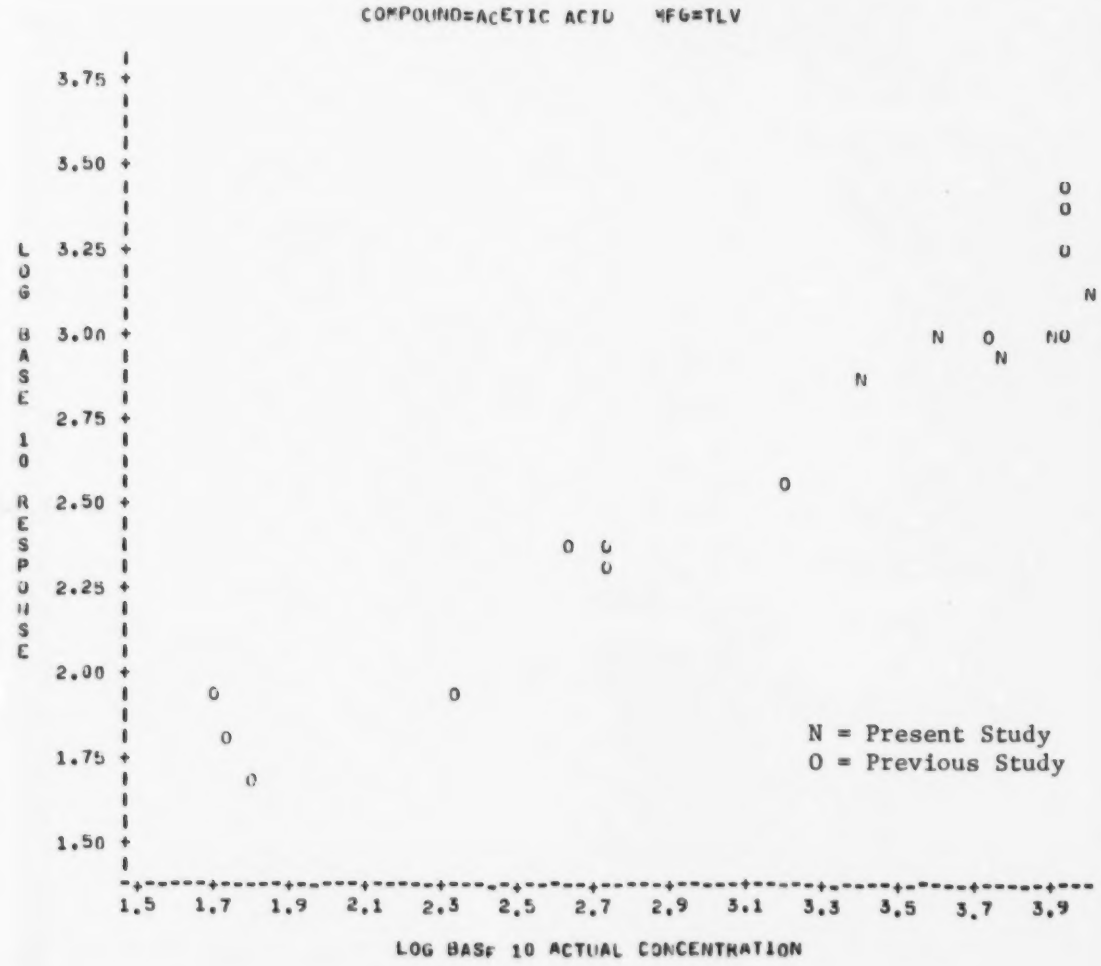


Figure 4-5. TLV Response to Acetic Acid

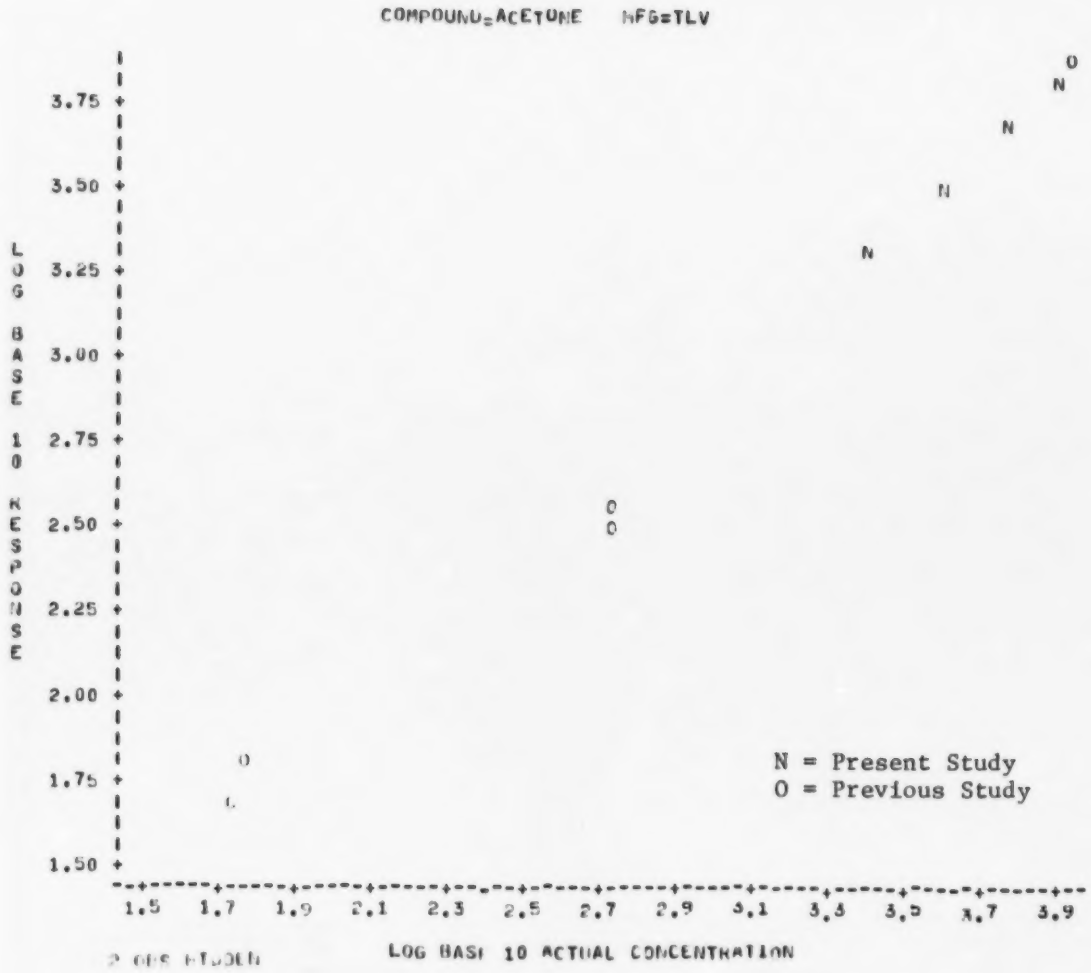


Figure 4-6. TLV Response to Acetone

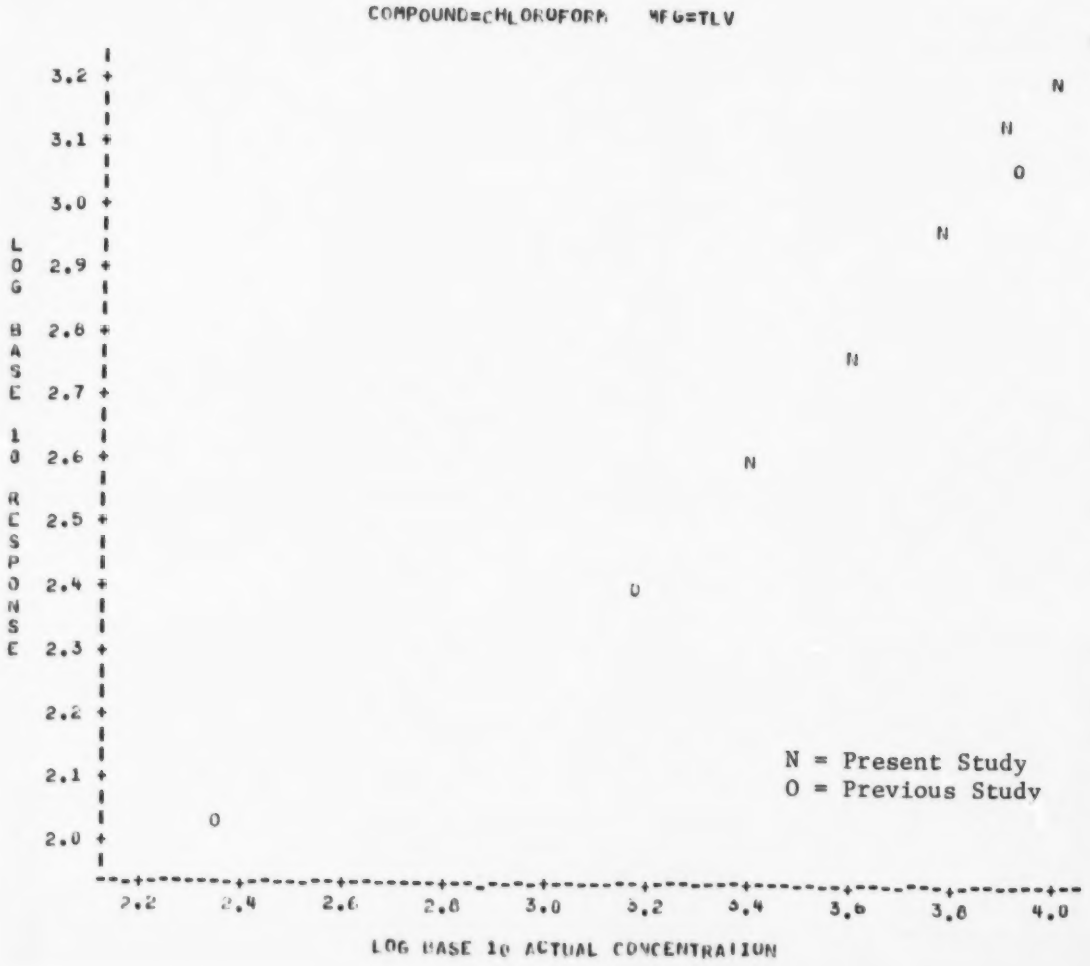


Figure 4-7. TLV Reponse to Chloroform

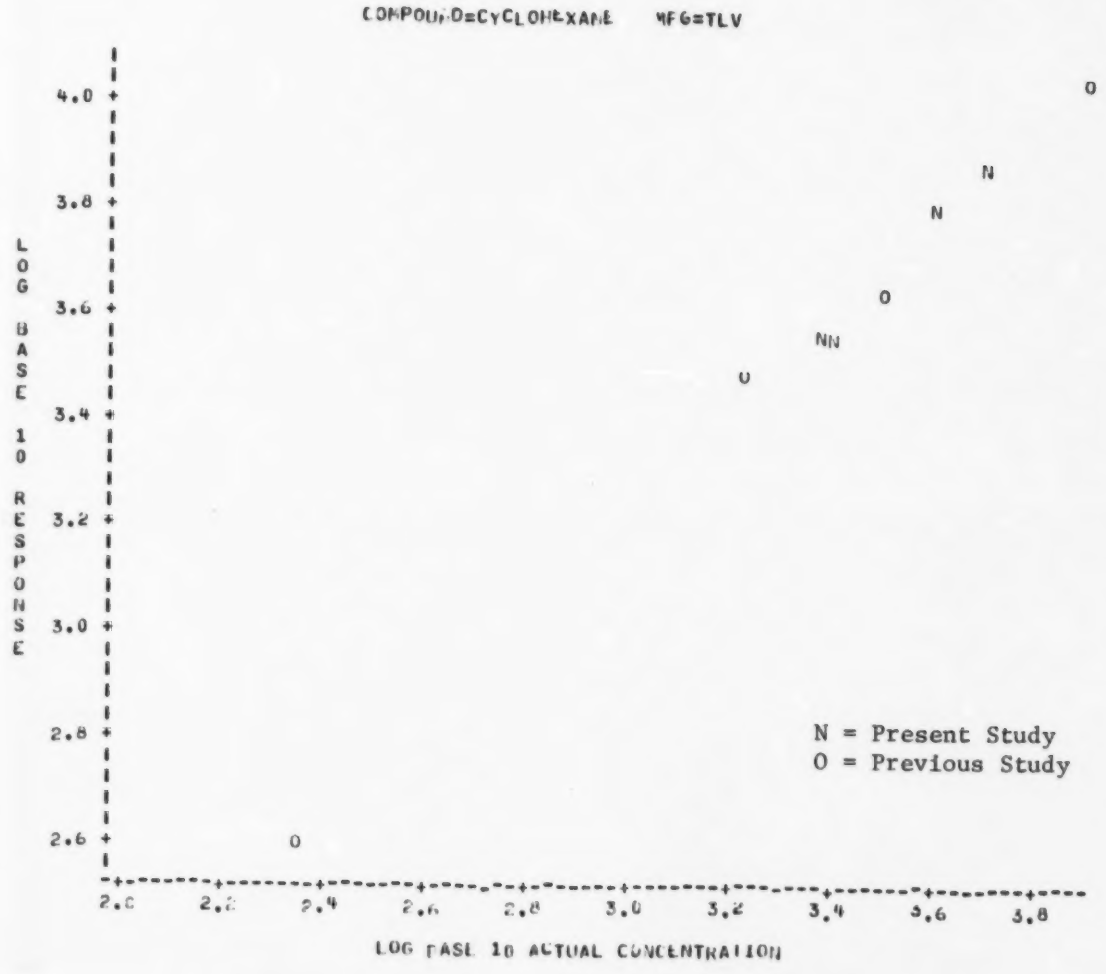


Figure 4-8. TLV Response to Cyclohexane

SECTION 5

REFERENCES

Brown, G. E., D. A. DuBose, W. R. Phillips, and G. E. Harris, 1980. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Chemicals. EPA 600/2-81-002, NTIS PB81-136194. Environmental Protection Agency, Research Triangle Park, N.C. 491 pp.

DuBose, D. A. and G. E. Harris, 1981. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Chemicals. EPA-600/2-81-051. U.S. Environmental Protection Agency, Research Triangle Park, N.C. 29 pp.

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(Please read Instructions on the reverse before completing)

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	6. PERFORMING ORGANIZATION CODE
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16. ABSTRACT The report gives the responses of two types of portable VOC analyzers (Century Systems OVA-108 and Bacharach TLV Sniffer), calibrated with methane and used to measure a variety of chemical vapor mixtures. Instrument response data for both binary and ternary mixtures of selected chemicals are presented. Various empirical models were evaluated to determine an appropriate method of estimating mixture concentration based on instrument response. The evaluation concluded that the instrument response for a mixture falls between the responses expected for the pure compounds in the mixture. Thus, an interpolation or weighted average model can be used to predict the response for mixtures based on known responses for individual chemicals. Both linear and logarithmic weighted average models are applied to the data and presented with estimates of accuracy. In general, these models predicted the instrument response to within 30% of the observed value.

17. KEY WORDS AND DOCUMENT ANALYSIS

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